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Air Emissions from the Treatment of Soils Contaminated with Petroleum Fuels and Other Substances

Radian Corp., Austin, TX

Prepared for:

Environmental Protection Agency, Research Triangle Park, NC

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Petroleum Products		Stationary Sources	11G	
Emission	Volatility	Contaminated Soils	14G	20M
Soils			08G, 08M	
Contamination				
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FINAL REPORT

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Washington, DC 20460

ABSTRACT

This document summarizes available information on air emissions from the treatment of soils contaminated with fuels. Soils contaminated by leaks or spills of fuel products, such as gasoline and jet fuel, are a nationwide concern. Air emissions during remediation are a potential problem due to the volatile nature of many of the fuel components and the remediation processes themselves, which may promote or result in contaminant transfer to the vapor-phase. Limited information is also included on air emissions from the treatment of soils contaminated with hazardous wastes.

The document will allow staff from State and local regulatory agencies, as well as staff from EPA regional offices, to assess the different options for cleaning up soil contaminated with fuels. Seven general remediation approaches are addressed in this report. For each approach, information is presented about the remediation process, the typical air emission species of concern and their release points, and the available air emissions data. Control technologies for each remediation approach are identified and their reported efficiencies are summarized. Cost data are given for each remediation approach and for its associated control technologies. Emission factors and other emission estimation procedures for each remediation approach are presented along with a brief case study.

This report was prepared in fulfillment of Contract No. 68-D0-0125, Work Assignment 25 by Radian Corporation, under the sponsorship of the U.S. Environmental Protection Agency. The report was revised under Contract No. 68-D1-0117, Work Assignment 31.

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Metric Conversions

Readers more familiar with the metric system may use the following factors to convert to that system.

Non-metric	Multiplied by	Yields Metric
MMBtu/hr	1054.35	MM J/hr
°F	0.555556 (°F - 32)	°C
ft	0.3048	m
acfm	0.028317	acmm
dscfm	0.028317	dscmm
gal	3.78541	L
hp	746	J/sec
in	2.54	cm
lb	0.453592	kg
mil	0.0254	mm
mile	1609.344	m
ton	0.907185	metric ton (1,000 kg)
cu yd	0.76455	m^3

EXECUTIVE SUMMARY

This document summarizes the available information on air emissions from the treatment of soils contaminated with fuels. It is intended to guide State and local air pollution control agencies in the evaluation of the air emission potential of treatment of contaminated soil and the cost-effectiveness of applicable emission control technologies. The scope was limited to the emissions of volatile organic compounds (VOCs); however, due to the limited data that were available, information was also included for the emissions of other organic compounds. This additional information is primarily from the treatment of soils contaminated with hazardous wastes.

Seven general approaches for the disposal or treatment of soils contaminated with gasoline, oil, or diesel fuel were identified:

- Excavation and removal;
- Thermal desorption;
- Soil vapor extraction (SVE);
- In-Situ biotreatment (e.g. landtreatment);
- Ex-Situ (batch) biotreatment;
- On-site incineration; and
- Soil washing/solvent extraction.

Each general approach may include several specific options. For example, thermal desorption may be performed in portable units designed specifically for soil treatment or in rotary drum aggregate dryers that are part of asphalt plants or other industrial facilities.

Literature pertaining to the emissions of volatile organic compounds (VOCs) for each remediation approach was identified and reviewed. The summarized information was organized into the same ten part format for each approach:

- Process description;
- Identification of air emission points;
- Identification of typical air emission species of concern;
- Summary of published air emissions data;
- Identification of applicable control technologies;
- Cost data for the overall remediation approach;
- Cost data for the emission controls;
- Equations and models for estimating VOC emissions;
- Case study of the use of the remediation approach; and
- References.

For most of the technologies examined, VOC emission estimates or measured data were found. Emission factors, in grams per hour, were identified or developed that are based on available data as well as assumed "typical" operating conditions for the remediation of relatively large sites. Cost data, in dollars per ton or cubic yard of soil treated, were obtained from a variety of sources, but data prior to 1986 were generally avoided because of the changes in remediation technology, standard operating practices, and regulations in recent years. All cost data were converted to 1991 dollars using a 5% annual escalation factor.

Certain limitations of the data presented in this document should be considered before extrapolations are made to a specific site under consideration. Any generalized guidance has inherent limitations due to the variety of site-specific and process-specific factors that may be encountered. Many of the cleanup processes are emerging technologies and have short operating histories. For these technologies, data on air emissions, treatment effectiveness, and costs are very limited. Furthermore, each site has its own unique obstacles to cleanup that may force modifications to the cleanup hardware or operating conditions. The development of typical air emission rates and emission factors applicable to the maximum number of site conditions and site locations required assumptions regarding the rate and scope of the clean-up effort, the type of fuel being treated, the number and nature of emission release points, and so on. The more a specific site differs from the assumed conditions, the less likely the generalized air emissions data will be applicable.

Data gaps were identified and suggestions for future research topics were given. In general, only limited information was found for air emissions from the treatment of contaminated soil. The need for more data is greatest for emerging technologies and those that are area sources of VOC emissions. The general needs are for more emissions data, more control cost and effectiveness data, and for accurate emission models. The most important research needs that were identified during this study were:

- VOC emission rate data for excavation;
- Theoretical models to estimate VOC emissions from excavation;
- Cost and effectiveness data of area source emission controls; and
- Fate studies for VOCs in biotreatment systems.

1.0 INTRODUCTION

1.1 Background

The Control Technology Center (CTC) at the U.S. Environmental Protection Agency (EPA) is responsible for supporting State and local air pollution control agencies in the implementation of their programs. As part of this support, the CTC provides control technology assessments to evaluate the control technologies available for reducing emissions from a particular type of source. The CTC typically provides expertise and information not otherwise available to the State or local agency.

The CTC has received requests from State and local regulatory agencies, as well as from EPA regional offices, regarding how to assess the different options for cleaning up contaminated soil. The requests have addressed a number of specific remediation techniques, such as the clean-up of soils using rotary drum dryers. Information is needed for estimating the potential air emissions from various types of processes and for determining what potential controls may be needed. While some guidance is currently available, it is dispersed among multiple documents.

The purpose of this project is to develop a procedure and guidance document for use by State and local regulatory agencies for evaluating the air emission potential and applicable control technologies for the treatment of contaminated soil. Radian Corporation, under contract to the U.S. EPA (Contract Number 68-DO-0125, Work Assignment 25 and Contract Number 68-D1-0117, Work Assignment 31) assisted the CTC in this effort. Existing guidance for how to assess both potential air emissions and available control technologies was identified. Examples of different clean-up operations were identified for soils contaminated with gasoline, diesel fuel, or fuel oil. Information on the kind of control technologies that are available and their expected range of capital and operating costs was also obtained.

1.2 Objectives

The specific objectives of this program were to:

- Identify options for the disposal/treatment of soils contaminated with gasoline, oil, or diesel fuel;
- Review the available literature pertaining to the emissions of volatile organic compounds (VOCs) for each clean-up option;
- Develop step-by-step instructions on how to estimate the VOC emissions from the various clean-up options;
- Identify applicable control technologies and compile ranges of capital and operating costs for each technology;
- Assess the uncertainty associated with the emission estimates and the need for any laboratory or field studies to collect data to address data gaps; and
- Summarize the information in a guidance document.

The clean-up options addressed in this document are:

- Excavation and removal;
- Thermal desorption (includes asphalt plants);
- Soil vapor extraction (SVE);
- In-Situ biotreatment (landtreatment);
- Ex-Situ (batch) biotreatment;
- On-site incineration; and
- Soil washing/solvent extraction.

1.3 Approach

The general approach was to perform a literature search and then to evaluate the collected documents. Over two hundred publications were reviewed and evaluated. Additional information was obtained from researchers active in this area.

For each of the identified remedial options, the literature was reviewed to develop a process flow diagram and identify emission points, as well as to analyze available air emissions data. For most of the technologies examined, VOC emission estimates or measured data were found. Where VOC data were limited, data for other types of organic compounds were also compiled. Emission factors were identified or developed that are based on available data as well as assumed "typical" operating conditions for the remediation of relatively large sites.

Much of the information in this document is based on and taken directly from the document titled, "Emission Factors for Superfund Remediation Technologies" (Thompson, Inglis, and Eklund, EPA-450/1-01-002, May 1991). Cost data were obtained from a variety of sources, but data from prior to 1986 were generally avoided due to the changes in remediation technology, standard operating practices, and regulations in recent years. All cost data were converted to 1991 dollars using a 5% annual escalation factor.

1.4 Frequency of Use of Various Remediation Options

The remediation options addressed in this document are all potentially suitable for use as part of the remediation process for soils contaminated with fuels. The various options, however, are not necessarily all equally cost-effective nor is their use equally widespread. EPA's Office of Underground Storage Tanks (OUST) has surveyed state agencies responsible for the cleanup of leaking underground storage tank (UST) sites to ascertain the frequency of use of various remediation options. The information is primarily derived from the remediation of UST sites contaminated with gasoline. This information is summarized in several figures.

Figure 1-1 shows the relative frequency of use of the major classes of remediation options. Landfilling (excavation and removal) is used somewhat more than half the time, with in-situ methods, thermal treatment, or land treatment also frequently used. Figure 1-2 provides more detail as to the type of in-situ, land treatment, and thermal treatment methods that are employed. For sites employing in-situ remediation, the exact technology used is undefined the majority of the time. It is assumed that soil vapor extraction is probably used in most of these cases. For applications of thermal treatment, thermal desorption is almost always employed and incineration is only very rarely used. Figure 1-3 shows the frequency of use of groundwater remediation technologies at UST sites. While these technologies are not part of the scope of this document, they are frequently used in conjunction with soil remediation technologies and the treatment of groundwater (e.g., by air stripping) may contribute to the overall levels of air emissions from the site. It is important to address all media when evaluating possible remediation scenarios.

1.5 Limitations of the Document

The initial review of the existing information showed that there was only limited published data. There was not adequate VOC air emissions data from remediation to assess the importance of fuel type, spill volume, the age of the spill, and the soil type as they relate to the combination of remediation and control technologies that are applied. Therefore, there was insufficient data to develop step-by-step estimation procedures and to assess the uncertainty associated with such estimates. Instead, the limited existing information was compiled to provide users with a summary of air emissions data. Information was included for VOC air emissions from the treatment of both soils contaminated with petroleum fuels and the treatment of hazardous waste to fill as many data gaps as possible.

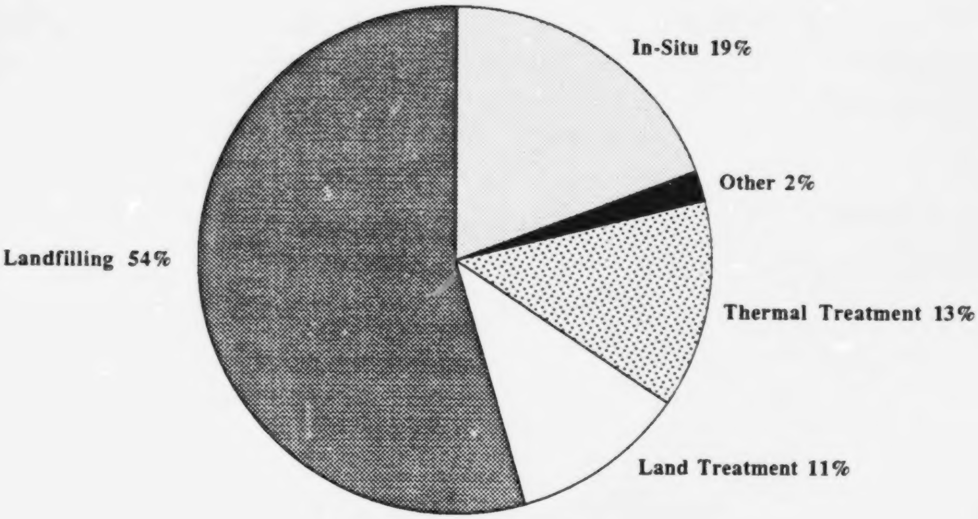
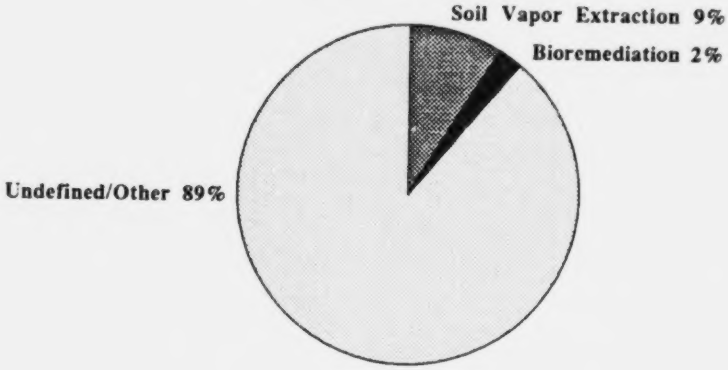


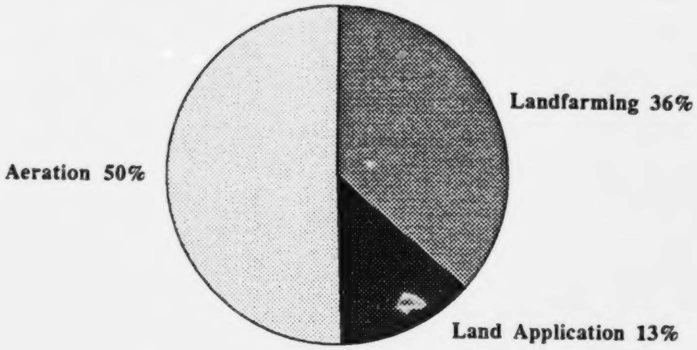
Figure 1-1. Relative Frequency of Use of Remediation Technologies at UST Sites

Source: EPA-OUST

In-Situ Technologies



Land Treatment Technologies



Thermal Treatment Technologies

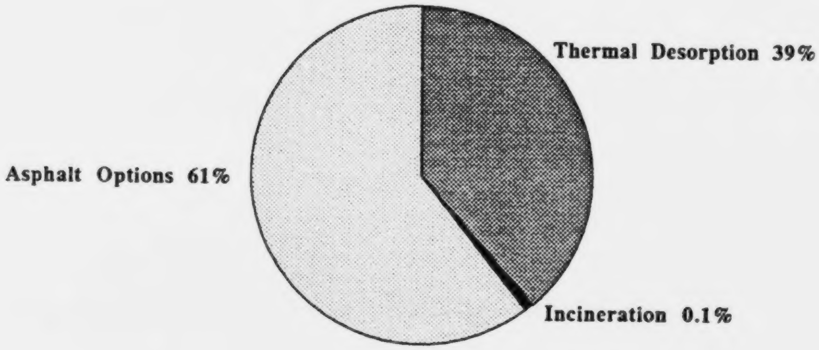


Figure 1-2. Relative Frequency of Use at UST Sites by Specific Technology

Source: EPA-OUST

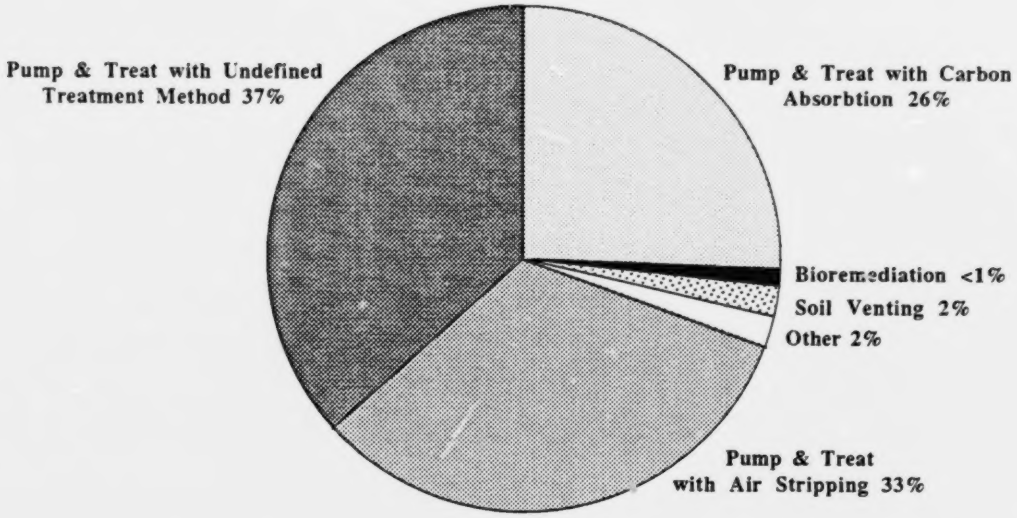


Figure 1-3. Relative Frequency of Use of Groundwater Remediation Technologies at UST Sites

Source: EPA-OUST

Generalized guidance for the remediation of soils contaminated with fuels has inherent limitations. Many of the cleanup processes are emerging technologies and have short operating histories. For these technologies, data on air emissions, treatment effectiveness, and costs are very limited. Furthermore, each site was its own unique obstacles to cleanup that may force modifications to the cleanup hardware or operating conditions.

The development of typical air emission rates and emission factors applicable to the maximum number of site conditions and site locations required assumptions regarding the rate and scope of the clean-up effort, the type of fuel being treated, the number and nature of emission release points, and so on. Assumptions were based on what is "typical" and "reasonable" for the remediation of relatively large sites. Obviously, the diverse nature of sites with fuel contamination will result in the information presented here being more applicable to some sites than others. A limited data set must be used to generalize about a wide-spectrum of process conditions.

The VOC air emissions data compiled in this document can be used for planning purposes and for comparison to permit applications, but the user must take into account the inherent limitations of the data and the limitations in extrapolating the data to fit the specific remediation scenario under consideration.

1.6 Organization of the Report

The remainder of this report is divided into nine sections. Section 2 presents a summary of the results obtained in this study. Sections 3 to 9 are each devoted to one of the seven cleanup technologies examined (excavation and removal, thermal desorption, soil vapor extraction, in-situ biotreatment, ex-situ biotreatment, incineration, and soil washing. Each of these sections follow the same ten-part format.

A number of appendices to the report are also given. Appendix A summarizes the properties and composition of various fuel types. Appendix B lists state-by-state clean-up requirements for fuel spills. Example calculations are given in Appendix C. Copies of selected references are given in Appendices D through F.

2.0 SUMMARY OF RESULTS

Typical treatment cost data are given in Table 2-1 for treatment operations with and without emission controls. The emission factors are based on "reasonable" operating conditions for the remediation of sites contaminated with petroleum fuels. These estimates may not be applicable to some clean-up programs. A range of costs are given in most cases and these estimates are considered to be the best available information in the literature. Since the cost estimates are not all based on the same remediation scenario, the data may not be directly comparable because the underlying assumptions of the volume of contaminated soil, the types and mass of contaminants that are present, the rate of treatment, the type of controls employed, etc. may vary.

There was insufficient data to provide estimated VOC emission factors based on starting soil contamination levels for the technologies discussed in this report. The discussions of each technology presented in subsequent sections summarize existing air emissions data. Concentration data (i.e. mass/volume of air) and emission rate data (mass/time) are given from various test programs, but these data are not necessarily directly comparable due to differences in the underlying assumptions.

Table 2-i.

Summary of Cost Information for the Treatment of Contaminated Soil

Technology	Estimated Treatment Cost ($/ton)	
	Controlled	Uncontrolled
Excavation and Removal	ND	75 - 500
Thermal Desorption	35 - 125	NA
Soil Vapor Extraction	52/ton of VOC	26/ton of VOC
In-Situ Biodegradation	NA	100
Ex-Situ Biodegradation	ND	70 - 130
On-Site Incineration	390-1020[a]	NA
Soil Washing	NA	53 - 215
Solvent Extraction	NA	105 - 525
Soil Flushing	NA	ND

[a] Assumes a small site and assumes incineration of hazardous waste, as opposed to incineration of soil contaminated with petroleum fuels.

ND = No estimate
NA = Not applicable

3.0 EXCAVATION AND REMOVAL

3.1 Process Description

Excavation and removal of soils contaminated with fuels is a common practice. Excavation and removal may be the selected remediation approach or it may be a necessary step in a remediation approach involving treatment. If removal is the preferred approach, the excavated soil is typically transported off-site for subsequent disposal at a landfill. If the soil contains large amounts of fuel or highly toxic contaminants, the soil may need to be treated off-site prior to final disposal. Excavation activities are also typically part of on-site treatment processes such as incineration, thermal desorption, batch biotreatment, landtreatment, and certain chemical and physical treatment methods. The soil is excavated and transported to the process unit and the treated soil is typically put back into place on the site. The information presented in this section for excavation and removal is generally applicable to all soils handling operations including excavation, dumping, grading, short-term storage, and sizing and feeding soil into treatment processes.

The magnitude of VOC emissions depends on a number of factors, including the type of compounds present in the waste, the concentration and distribution of the compounds, and the porosity and moisture content of the soil. The key operational parameters are the duration and vigorousness of the handling, and the size of equipment used. The longer or more energetic the moving and handling, the greater likelihood that organic compounds will be volatilized. The equipment size influences volatilization by affecting the mean distance a volatilized molecule has to travel to reach the air/solid interface at the surface of the soil. In general, the larger the volumes of material being handled per unit operation, the lower the percentage of VOCs that are stripped from the soil. Control technologies for large area sources such as excavation are relatively difficult to apply and are often much less effective than controls for point sources.

The relative advantages of excavation and removal over other remediation approaches are that:

1) Earth-moving equipment and trained operators are widely available;

2) Large volumes of soil can be quickly moved in a cost-effective manner; and

3) Residual contamination remaining at the site is minimal.

The major disadvantages of excavation and removal versus other remediation approaches are that:

1) The magnitude of air emissions may be high;
2) Air emissions from excavation are difficult to control; and
3) The contaminants are only removed, they are not destroyed.

The success of excavation and removal for a given application depends on numerous factors with the three key criteria being: 1) the nature of the contamination; 2) the operating practices followed; and 3) the proximity of sensitive receptors. Each of these criteria is described below.

As previously discussed, spills or leaks of fuels typically involve liquids containing dozens of different constituents. Excavation and removal is generally a viable option, except for those cases where air emissions potentially pose an unacceptable risk. For example, soil containing percent levels of benzene or other volatile carcinogens would almost certainly pose a large risk to on-site workers and the surrounding populace if it were to be excavated. In-situ remediation methods, such as soil vapor extraction, would be preferable for such a site, either in lieu of excavation or prior to excavation to reduce the emissions potential.

The magnitude of emissions from soils handling operations will vary with the operating conditions. Add-on control technologies are available for minimizing VOC emissions, but they are relatively ineffective and costly to implement. VOC emission control can also be achieved by controlling the operating conditions within preset parameters. The rate of excavation and dumping, the drop height, the amount of exposed surface area, the length of time that the soil is exposed, the shape of the storage piles, and the dryness of the surface soil layers will all influence the levels of VOC emissions. Large reductions in emissions can be achieved by identifying and operating within acceptable ranges of operating conditions.

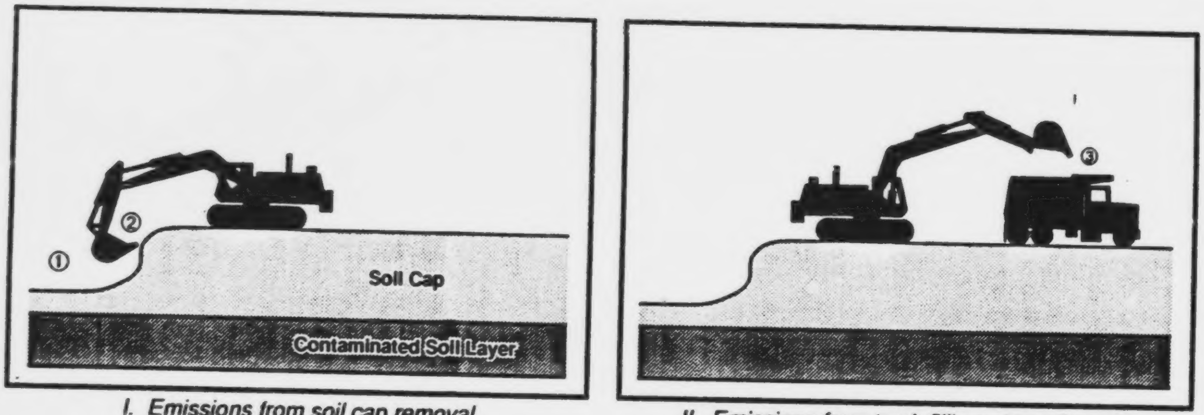
Since some release of volatile contaminants is inevitable during excavation and removal unless extreme measures are taken (e.g. enclose the remediation within a dome), the proximity of downwind receptors (i.e. people) will influence whether or not excavation is an acceptable option. Excavation of contaminated areas that abut residential areas, schoolyards, etc. may require more extensive controls, relocation of the affected population, or remediation only during certain periods (e.g. summertime for school sites).

3.2 Identification of Air Emission Points

VOC emissions from handling operations result from the exchange of contaminant-laden soil-pore gas with the atmosphere when soil is disturbed and from diffusion of contaminants through the soil. There are several potential emission points involved in excavation as shown in Figure 3-1; all are considered to be fugitive area sources. For excavation, the main emission points of concern are emissions from:

- exposed waste in the excavation pit;
- material as it is dumped from the excavation bucket; and
- waste/soil in short-term storage piles.

In addition, emissions of VOC, particulate matter, nitrogen oxides, etc. will also occur from the earth-moving equipment.

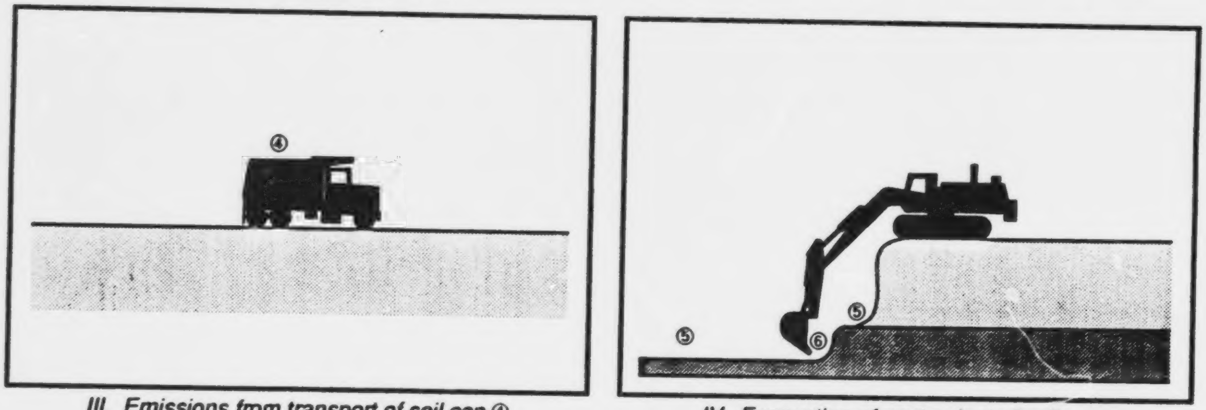


I. Emissions from soil cap removal

① Emissions from soil cap excavation

② Emissions from soil cap in bucket

II. Emissions from truck filling with soil cap ③



III. Emissions from transport of soil cap ④

IV. Excavation of contaminated soil zone

⑤ Emissions from exposed contaminated soil zone

⑥ Emissions from excavation of contaminated soil

Figure 3-1. Summary of Air Emission Points For Excavation and Removal.

Source: Saunders, 1990.

3.3 Typical Air Emission Species of Concern

The emissions of concern from soils handling operations such as excavation can be any contaminant that is present in the soil. Relatively large amounts of volatile organic compounds (VOCs) may be released from soil during handling, so VOCs are typically the emissions of most concern. Emissions of particulate matter and associated metals and semi-volatile compounds may be of concern at some sites.

3.4 Summary Of Air Emissions Data

Very limited references with VOC emissions or emission rate data for excavation were identified in the literature search performed for this project. The process of measuring emission rates from dynamic processes, such as excavation, is difficult and costly, and so has rarely been attempted.

Volume III of the Series of Air-Superfund Guidance Manuals (Eklund, et al, 1989) for estimating clean-up emissions indicates that soils handling operations such as excavation increase VOC emission rates from contaminated soil over baseline rates. The increase in emissions is typically a factor of ten or more, and the increased emission rate decays exponentially back to near the baseline rate over short time periods (e.g. 4 days). A database of baseline emission rate measurement data (Eklund, et al, 1991) is available.

Emission rate measurements have been made at two sites (Eklund, et al, 1990). Excavation decreased the soil moisture content by 35% to 56% and tended to somewhat decrease (e.g. -13%) the dry bulk density of the soil. Measured emission rates were as high as 4 g/min for specific compounds. These emissions were from both the excavation and dumping processes. Excavation resulted in most of the mass of various volatile compounds being stripped from the soil, based on a comparison of measured total emissions versus the mass of these same contaminants in the soil (calculated from soil concentration data). This was true for both sites, despite differences in soil concentrations and soil type. For sites with medium to high ppm-levels of contamination and/or wet soil, a lower percentage of contaminants would be stripped from the soil during excavation.

Theoretical models for estimating emissions (Eklund 1992a) indicate that about 70% of the mass of a volatile compound such as xylene is emitted during excavation of soil with a starting contaminant concentration of 1 ppm under the assumed typical conditions. Another theoretical study (Saunders, 1990) of soils handling emissions estimated that relative to excavation, other soils handling operations would have the following emissions: 1) Truck Filling - 0.58; 2) Transport - 5.23; and 3) Exposed soil - 1.47 (emissions/excavation emissions).

Field experience indicates that actual emissions may be substantially lower than the stripping percentages discussed above. For dry, porous soils containing low ppb levels of contaminants it can be assumed that most or all of the more volatile VOCs will be lost to the atmosphere during soils handling. For sites with moist soils and ppm levels of contaminants, however, a reasonable assumption may be that only 5 to 10% of the VOCs are emitted to the atmosphere during each handling step. More measurement data are needed to support these assumptions.

No valid emission factors were found. A theoretical study of the emissions from the clean-up of leaking underground storage tank sites (U.S. EPA-OUST, 1989) estimated that emissions from storage piles of contaminated soil with a surface area of 186 m^2 (2,000 ft^2) were:

Average Benzene Emission Rate (lb/hr)*	1
Total Benzene Emissions (lb)	336
Average VOC Emission Rate (lb/hr)	50
Total VOC Emissions (lb)	16,800

* Readers more familiar with the metric system may use the factors listed at the end of the front matter to convert to that system.

The total emissions are based on a two-week time period. Emissions from the actual excavation process, as opposed to soils storage, were not estimated.

3.5 Identification of Applicable Control Technologies

A number of methods are available for controlling VOC and particulate matter emissions from soils. In general, any method designed primarily for particulate control will also reduce VOC emissions and vice versa. Compared to point source controls, VOC emission controls for excavation and other area sources are difficult to implement and only moderately effective. Controls such as water sprays or foams will alter the percent moisture, bulk density, and average heating value of the soil and may impact treatment and disposal options.

VOC emission controls for soil area sources are described below including:

- Covers and physical barriers;
- Temporary and long-term foam covers;
- Water sprays;
- Operational controls;
- Complete enclosures; and
- Wind Barriers.

Additional information is given in Eklund, et al., 1992b.

3.5.1 Covers and Physical Barriers

The most commonly used VOC control approach for area sources is the use of covers to provide a physical barrier to vapor transport. The simplest barrier is the use of relatively clean soil as a cover for contaminated soil. The soil layer increases the necessary transport distance for vapor diffusion and thus greatly reduces, at least temporarily, the emission rate. Soil covers are widely used at sanitary landfills to control the emissions of odorous compounds and to control wind-borne pollution. The effectiveness of soil covers will depend on the depth of the cover and the percent of contaminated soil that can be covered. Measured emission rates may be substantially reduced (e.g., >95%) by the addition of compacted soil (Suder and Schmidt, 1992); however, lateral migration of VOCs may still occur. Soil covers will be less effective over long time periods and their use will tend to increase the total volume and mass of material that must be treated.

Synthetic covers are typically used to control VOC emissions from excavated soil in short-term storage piles. Synthetic covers are also widely used to control VOC emissions during transport by rail or truck. The cover may be thin (4-6 mil) plastic sheeting or relatively thick (30-40 mil) plastic sheeting or geotextile material. The resistance of various polymers to chemicals, weather, gas permeability, and tears is documented (Landeeth, et al., 1983). The barrier material is available in large rolls and can be quickly applied to even large soil piles. The barrier must be secured against wind. Application of the barrier generally forces on-site workers to come in contact with the waste. The barrier can be left in place indefinitely, though physical and photodegradation of the polymer will tend to limit the effective lifetime of thin barriers to a few weeks. The effectiveness of the cover will depend on its permeability to the vapors that are present and the percentage of the soil pile that is adequately covered. Laboratory measurements of a 20 mil PVC membrane showed relatively poor performance for limiting vapor diffusion (Springer, et al, 1986). The PVC membrane proved to be only as effective as a covering of a few inches of porous soil.

Numerous mulch materials, such as sawdust, wood chips, straw, and wood fibers can also be used as a cover for soil undergoing long-term storage (U.S. EPA, 1991). The mulch acts primarily to control diffusion by insulating the soil surface and thereby lowering the soil temperature. The mulch material will also limit diffusion somewhat if it is used as a cover, but if mixed in with the contaminated soil the mulch will generally increase the porosity of the soil and thereby increase the emission rate. The mulch will also increase the volume and mass of contaminated material to be treated or disposed.

3.5.2 Temporary and Long-Term Foam Covers

Modified fire-fighting foams are commonly used to control VOC emissions during the remediation of hazardous waste sites containing volatile toxic compounds. At least six types of foam products are available (Evans and Carroll, 1986) from vendors such as Rusmar and 3M. The different foams vary in their compatibility and effectiveness for various classes of contaminants. Specialized equipment is available for applying foams over large areas. The foam is applied to a depth of 6-18 inches and coverage rates of 100 m^2/min are possible. The liquid foam concentrate is applied via an air-aspirating nozzle or chute. The degree of expansion (how many gallons of foam produced from a gallon of liquid concentrate) can be high (250:1), low (20:1), or medium.

Two general types of foams are used: temporary and long-term. The temporary foams provide coverage for up to an hour, at which time 25% or more of the liquid incorporated in the foam will have been released. Long-term foams contain a stabilizing additive to extend the useful life of the foam to days or even months. The effectiveness of foams is quite high for the areas that are covered. Short-term emission reductions of 75% to 95% (for total paraffins and total aromatics, respectively) have been measured in the field over 20 minute time periods (Alm, et al, 1987). Emission reductions for total VOCs of 99% to 100% using stabilized foam have been measured in the field over 24-hour time periods (Alm, et al, 1987).

The two primary advantages of foams are that they can be highly effective and they can be applied directly to the backhoe bucket and the exposed contaminated soil. There are several disadvantages to foams worth consideration. The thick layers of foam required for emissions control can be applied more effectively to horizontal surfaces than to vertical surfaces such as the sides of the excavation pit. Incomplete coverage of the emitting surfaces will markedly decrease the effectiveness of the controls. The foam concentrates are usually over 90% water and the addition of this water increases the weight of the soil, makes it more difficult to handle, and makes it less amenable to thermal treatment. Specialized foam application equipment and a large supply of foam concentrate are needed. The foam is difficult to apply on windy days. Frequent application or re-application of the foam may be necessary.

3.5.3 Water Sprays

Water sprays are a commonly used control method for particulate matter (PM) emissions. The addition of dust control chemicals such as polymers or acrylics to the water increases the effectiveness of the spraying. The water added to the soil will decrease the air-filled porosity of the soil and will also tend to cool the surface soil temperature. The reduction in vapor transport will diminish VOC emissions, though the effectiveness of water sprays for VOC control is not documented. Water sprays are certainly much less effective than water-based foams, and they have essentially the same limitations as those listed above for foams.

3.5.4 Operational Controls

Operational controls can be effective in minimizing VOC emissions. These controls may involve controlling the rate of excavation, the amount of contaminated soil area that is exposed, and the duration that soil piles are left uncovered. The timing of excavation can also be important. Scheduling excavation during times of the day or seasons of the year when wind speeds and temperatures are low can reduce emissions. Stagnant wind conditions, however, may lead to unacceptable ambient air concentrations at the work site. The work can also be scheduled to avoid seasons with dry soil conditions to further minimize emissions.

3.5.5 Complete Enclosures

If warranted, complete enclosure of the excavation site can be accomplished to minimize VOC emissions. The enclosure acts to collect any emissions, which can then be vented to some type of control device suitable for point sources (see Section 5.5). The enclosure may be either air supported or self supported. Self-supported domes are more practical if trucks or other heavy equipment must regularly enter and leave the structure. If properly designed and operated, the enclosure may reduce VOC emissions to negligible levels.

There are severe limitations that limit the use of complete enclosures to the few sites where other control options are not acceptable. The capital cost of the structure is relatively high. Operating costs can also be very high if large volumes of air must be treated and exhausted to keep the concentrations of contaminants in the atmosphere within the dome at levels that are safe for the workers. The use of a complete enclosure will generally require the workers inside the structure to work under Level B or C safety requirements. Due to the greenhouse effect, the air temperatures within the structure may be high. The added safety requirements along with the time delays in transferring trucks in and out of the structure will extend the time to complete the excavation and thereby increase the cost.

3.5.6 Wind Barriers

For small work areas, the use of wind barriers can reduce VOC emissions by lowering the effective wind speed at the soil surface. Commercial, porous wind fence material that is typically used for dust control has been found to be more effective than solid fence material (Springer, et al, 1986). For larger working areas, fencing is less practical.

VOC (and PM) emissions from storage piles can be minimized by controlling the placement and shape of the piles. When feasible, the piles can be placed in areas shielded from the prevailing winds at the site. The amount of surface area can be minimized for the given volume of soil by shaping the pile. The orientation of the pile will affect the wind velocity across the pile with the lowest windspeed occurring when the length of the pile is perpendicular to the prevailing wind direction.

3.6 Costs For Remediation

The total costs for the treatment of contaminated soil by excavation and removal will be the sum of the costs for excavation, transport, and treatment or disposal. The total costs will vary widely and are primarily dependent on the disposal or treatment costs. Total costs per ton may range from $75 to $500 or more, for excavation and off-site disposal. All costs shown below have been converted to 1991 dollars using a 5% annual escalation factor. The cost per cubic yard will tend to increase for smaller levels of effort such as the cleanup of a typical LUST site.

Standard costs for earth-moving activities are available (Means, 1991). Estimates of excavation costs for petroleum contaminated soils are in the range of $2.50 to $6.00 per ton (Troxler, et al., 1992). The costs of excavation will depend the level of personal protective equipment required by the operator and on-site workers. Costs to excavate soil contaminated with hazardous wastes for different safety levels are (Lippitt, et al, 1986):

No hazard	\$22.37 +/- 18.80 per m^3 (\$1/m^3 = \$1.30/yd^3);
Level D	\$74.73 +/- 56.19 per m^3;
Level C	\$91.32 +/- 83.79 per m^3;
Level B	\$117.10 +/- 85.57 per m^3; and
Level A	\$133.38 +/- 96.38 per m^3.

Published cost estimates for excavation of soil contaminated with hazardous wastes vary widely. The estimated cost to excavate and load sixteen million cubic yards at the Rocky Mountain Arsenal was only \$6/yd^3 (U.S. GAO, 1986). The cost to excavate large volumes of soils contaminated with explosives has been estimated to be \$11.14/ton, or about \$13.92/yd^3 (TVA, 1990). This cost comprised 79% labor, 7% operating expenses, 10% equipment expense, and 4% for site reclamation. The cost to excavate large volumes of soils at another DOD site were estimated per cubic yard to be (Cullinane, et al, 1986):

Dry excavation	\$5.36 (per yd^3)
Wet excavation	\$10.72
Site grading and revegetation	\$1.66
Site grading	\$1.15
Backfilling with clean soil	\$25.84

Cost estimates for transportation of petroleum contaminated soils range from \$0.08 to \$0.15 per ton per mile (Troxler, et al., 1992). Vendor quotes for off-site transportation of soil contaminated with hazardous wastes typically range from \$2.50 to \$5/yd^3 per mile, though they may be higher under some site-specific conditions. Costs for transporting soil will be lower for on-site work and will be lower for off-site transport if it is not necessary to follow the procedures typically employed for transporting soils contaminated with hazardous wastes. Published cost estimates for off-site transport include an estimate of about \$3.80/yd^3 per mile (Cullinane, et al, 1986) and an average from ten sites of \$0.25/ton per mile (Yang, et al, 1987). A cubic yard of soil can be assumed to weigh about 2500 pounds.

Disposal costs are highly dependent on the amount and nature of contamination present in the soil. Vendor quotes for disposal are typically \$250 to \$350/yd^3 of soil. Published estimates (Cullinane, et al, 1986) include costs of \$38/yd^3 for disposal in a sanitary landfill and \$160/yd^3 for disposal in a RCRA landfill.

3.7 Costs For Emission Controls

Costs for VOC controls for excavation are not widely available in the literature. The following summary information was obtained from Eklund, et al., 1992b:

Control	Material Cost ($/M^2 except as noted)	Comments
Clay	$4.15	Covers, mat, and membrane
Soil	$1.33	Assume 6" deep; does not include soil transport
Wood chips, plastic net	$0.50	Chip costs vary with site
Synthetic Cover	$4.40	Assume 45 ml thickness
Short-term foam	$0.04	Assume 2.5" thick, $0.7/M^3 foam*
Long-term foam	$0.13	Assume 1.5" thick, $3.3/M^3 foam*
Wind screen	$40/M	Per linear meter
Water Spray	$0.001 (varies)	Assuming municipal water cost of $1/$1,000 L. Water requires constant re-application. Water truck rental: $500/week.
Additives:		
Surfactant	$0.65	Costs vary with chemical use
Hygro Salt	$2.58	
Bitu/Adhes.	$0.02	

3.8 Equations and Models For Estimating VOC Emissions

The factors that govern excavation emissions are very complex. During excavation, the physical properties of the soil that control the vapor transport rate (e.g. air-filled porosity) are changing with time and the concentration of contaminants may be rapidly decreasing. Predictive equations for estimating VOC emissions from excavation have been developed by the U.S. EPA. The predictive equations require assumptions about the size of each scoop of soil, the dimensions of the soil scoops and the excavation pit, and the shape of the soil after it is dumped. Further assumptions are required about the air and soil temperatures and the length of time that dumped soil is exposed before it is covered with more soil or with an emissions barrier.

Since it is rarely feasible or efficient to dig soil and immediately transfer the soil directly to transport vehicles or treatment systems, any estimation procedure must account for each event in which the soil is handled. In most cases, soil will be excavated and placed into a temporary holding area and then handled one to two more times on-site. Elevated levels of VOC emissions are possible each time the soil is handled. When estimating emissions from sequential soil handling steps, it is important to adjust the starting concentrations for each step to account for contaminants emitted during prior steps.

The equations used are shown below. The average emission rate (g/sec) from excavation is equal to the sum of emission rates from the soil pore space and from diffusion:

$$ER = ER_{PS} + ER_{DIFF} \qquad \text{(Eq. 3-1)}$$

$$ER_{PS} = \frac{PMW\ 10^6\ E_a\ Q\ ExC}{R\ T} \qquad \text{(Eq. 3-2)}$$

$$ER_{DIFF} = \frac{(C)(10{,}000)(SA)}{\left(\frac{E_a}{K_{eq}\ k_g}\right) + \left(\frac{\pi t}{D_e\ K_{eq}}\right)^{\frac{1}{2}}} \qquad \text{(Eq. 3-3)}$$

All variables are defined in Table 3-1. Also shown in Table 3-1 are the units of each variable and a typical default value to use if valid field data are not available. Equation 3-2 is based on the assumption that the soil pore gas is saturated with the compound of interest. If this is not the case, then Equation 3-2 may overpredict the emission rate.

Table 3-1.

Input Variables for Emission Equations

Variable	Definition	Units	Default Value
P	Vapor pressure	mm Hg	35
MW	Molecular weight	g/g-mol	100
R	Gas constant	mm Hg-cm^3/g-mol$^\circ$K	62,361
T	Temperature	Degrees Kelvin	298
E_a	Air-filled porosity	Dimensionless	0.440
S_v	Volume of soil moved	m^3	150
Q	Excavation rate	m^3/sec	0.042
10^6	Conversion factor	cm^3/m^3	--
ExC	Soil-gas to atmosphere	Dimensionless	0.33
C	Concentration in bulk soil[a]	g/cm^3	1.35×10^{-4}
10,000	Conversion factor	cm^2/m^2	--
SA	Emitting surface area	m^2	290
K_{eq}	Equilibrium coefficient	Dimensionless	0.613
k_g	Gas-phase mass transfer coefficient	cm/sec	0.15
π	Pi	Dimensionless	3.14
t	Time	sec	60
D_e	Effective diffusivity in air	cm^2/sec	0.0269
M	Total mass of contaminant	g	--
Other Variables Required to Calculate Certain Variables Listed Above			
t_{sv}	Time to excavate a given volume of soil	sec	--
β	Bulk density	g/cm^3	1.5
ρ	Particle density	g/cm^3	2.65
D_a	Diffusivity in air	cm^2/sec	0.1
U	Wind speed	m/sec	2.0
μ_a	Viscosity of air	g/cm-sec	1.81×10^{-4}
ρ_a	Density of air	g/cm^3	0.0012
d_e	Diameter of emitting area	m	24

[a] Soil concentration data is typically available as ppm or μg/g. This value can be multiplied by the bulk density of the soil (g/cm^3) and by a conversion factor of 10^{-6} (g/μg) to yield units of g/cm^3.

The output from Equation 3-2 should be multiplied by the duration of excavation and compared to the total mass of contaminants present in the soil:

$$M = C * S_V * 10^6 \frac{cm^3}{m^3} \qquad \text{(Eq. 3-4)}$$

where: M = Total mass of contaminant in a given volume of soil (g).

If Equation 3-2 gives a value that exceeds one-third of C_{TOT}, then the following equation should be substituted for Equation 3-2:

$$ER_{PS} = M * \frac{0.33}{t_{sv}} \qquad \text{(Eq. 3-5)}$$

where: t_{sv} = Time to excavate a given volume of soil (sec).

Equation 3-3 can be used to estimate VOC emissions from storage piles.

3.9 Case Study

No suitable case study exists for excavation. Studies that have valid data for emissions, control efficiencies, and costs are referenced above in the applicable subsections.

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4.0 THERMAL DESORPTION

This section discusses both mobile and stationary process units designed for soil remediation and the use of asphalt aggregate dryers for soil remediation. Data are included in this section for the treatment of soil contaminated with petroleum fuels and soil contaminated with hazardous wastes.

4.1 Process Description

In the thermal desorption process, volatile and semi-volatile contaminants are removed from soils, sediments, slurries, and filter cakes. This process typically operates at temperatures of 350°-700°F but may operate in the 200°-1200°F temperature range. It is often referred to as low temperature thermal desorption to differentiate it from incineration. At these lower temperatures, thermal desorption promotes physical separation of the components rather than combustion. Contaminated soil is removed from the ground and transferred to treatment units, making this an *ex situ* process. Direct or indirect heat exchange vaporizes the organic compounds producing an off-gas that is typically treated before being vented to the atmosphere (Vatavuk, 1990). The best single source of information on thermal desorption is contained in an EPA Guidance Document currently being prepared (Troxler, et al. 1992). The best currently available source of information is an engineering bulletin prepared by the U.S. EPA (U.S. EPA, 1991), which is included as Appendix D to this report.

After it is excavated, the waste material is screened to remove objects greater than 1.5" to 3.0" in diameter (de Percin, 1991a). In general, four desorber designs are used: rotary dryer, asphalt plant aggregate dryer, thermal screw, and conveyor furnace. The treatment systems include both mobile and stationary process units designed specifically for treating soil and asphalt aggregate dryers which can be adapted to treat soils. Typical specifications for thermal desorption systems are shown in Table 4-1.

Table 4-1.

Comparison of Features of Thermal Desorption and Offgas Treatment Systems

	Rotary Dryer	Asphalt Plant	Thermal Screw	Conveyor Furnace
Estimated number of systems	40-60	100-150	18-22	1
Estimated number of contractors	20-30	No estimate	9	–
Mobility	Fixed and mobile	Fixed	Mobile	Mobile
Typical site size (tons)	500-25,000	0-10,000	500-5,000	500-5,000
Soil throughput (tons/hour)	10-50	25-100	3-15	5-10
Maximum soil feed size (inches)	2-3	2-3	1-2	1-2
Heat transfer method	Direct	Direct	Indirect	Direct
Soil mixing method	Shell rotation and lifters	Shell rotation and lifters	Auger	Soil agitators
Discharge soil temperature (°F)	300-600[a] 600-1,200[b]	300-600	300-500[c] 600-900[d] 1,000-1,600[e]	300-800
Soil residence time (minutes)	3-7	3-7	30-70	3-10
Thermal desorber exhaust gas temperature (°F)	500-850[a] 800-1,000[b]	500-850	300	1,000-1,200
Gas/solids flow	Co-current or counter-current	Co-current or counter-current	Not applicable	Counter-current
Atmosphere	Oxidative	Oxidative	Inert	Oxidative
Afterburner temperature (°F)	1,400-1,800	1,400-1,800[f]	Generally not used	1,400-1,800
Maximum thermal duty (MM Btu/hr)[g]	10-100	50-100	7-10	10
Heatup time from cold condition (hours)	0.5-1.0	0.5-1.0	Not reported	0.5-1.0
Cool down time from hot condition (hours)	1.0-2.0	1.0-2.0	Not reported	Not reported
Total Petroleum Hydrocarbons				
Initial concentration (mg/kg)	800-35,000	500-25,000[h]	60-50,000	5,000
Final concentration (mg/kg)	<10-300	<20[h]	ND-5,500	<10.0
Removal efficiency (%)	95.0-99.9	Not reported	64-99	>99.9
BTEX				
Initial concentration (mg/kg)	NR	Not reported	155	Not reported
Final concentration (mg/kg)	<1.0	Not reported	<1.0	<0.01
Removal efficiency (%)	NR	Not reported	>99	Not reported

[a] Carbon steel materials of construction
[b] Alloy materials of construction
[c] Hot oil heat transfer system
[d] Molten salt heat transfer system
[e] Electrically heated system
[f] Not used on all systems
[g] Total duty of thermal desorber plus afterburner
[h] Vendor information: Soil Purification, Inc.

Source: Troxler, personal communication, 1991.

Because thermal desorbers may operate near or above 1000°F, some pyrolysis and oxidation may occur in addition to the vaporization of water and organic compounds. Collection and control equipment such as afterburners, fabric filters, activated carbon, or condensers prevent the release of the contaminants to the atmosphere (de Percin, 1991a). Various types of thermal desorption systems can produce up to nine process residual streams: treated soil, oversized media rejects, condensed contaminants, water, particulate control dust, clean off-gas, phase separator sludge, aqueous phase spent carbon, and vapor phase spent carbon (de Percin, 1991b).

The final temperature is a function of residence time and heat transfer and is the principle variable in controlling effectiveness. A study by the Hazardous Waste Research and Information Center and the Gas Research Institute showed that temperatures and residence times effective in bench-scale systems also proved effective in pilot-scale systems. Such data support the use of a bench-scale test to determine the best residence time and temperature variables as well as whether the thermal desorption process will suitably treat the waste (de Percin, 1991a). The typical treatment temperature range for petroleum fuels from leaking underground storage tanks (LUST) sites is 400°F to 900°F. For the treatment of soils containing pesticides, dioxins, and PCB's, temperatures should exceed 850°F (de Percin, 1991c). The distillation temperature range will vary with the type of fuel contaminated soil as shown in Figure 4-1.

Thermal desorbers effectively treat soils, sludges and filter cakes and remove volatile and semi-volatile organic compounds. Some higher boiling point substances such as polychlorinated biphenyls (PCB's) and dioxins may also be removed (if present). Inorganic compounds are not easily removed with this process, although some relatively volatile metals such as mercury may be volatilized. Temperatures reached in thermal desorbers generally do not oxidize metals (de Percin, 1991a).

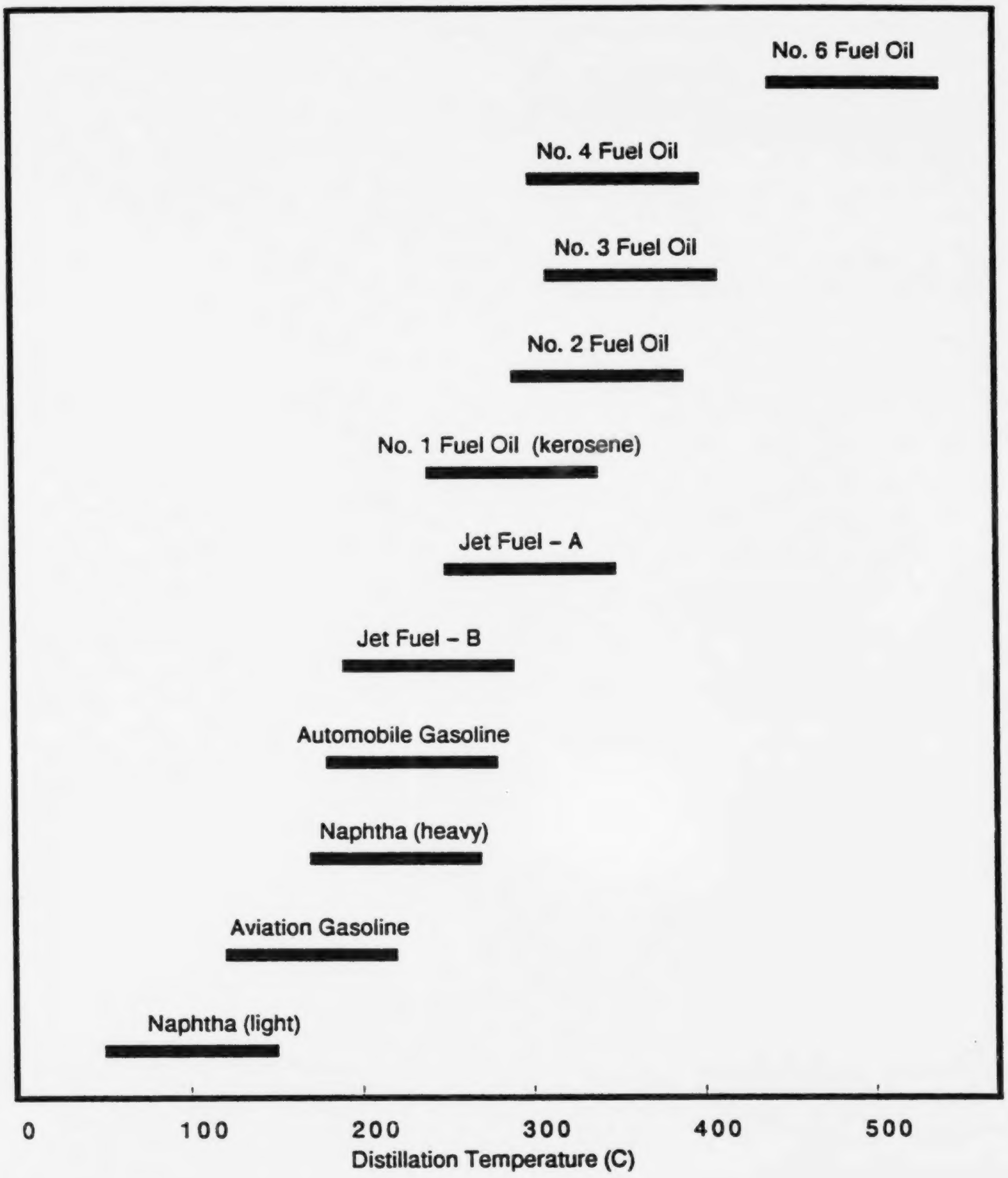

Figure 4-1. Soil Treatment Temperature Guide.

Source: Troxler, et al. 1990

The soil is most effectively treated if it contains moisture level within a specified range due to the cost of treating waste with a high water content. Typical acceptable moisture ranges for rotary dryers and asphalt kilns are 10-30%, (Troxler, personal communication, 1991 and SPI, 1991), while thermal screw systems can accommodate a higher water loading of 30-80%. For VOC removal, soils ideally should contain 10-15% moisture since water vapor carries out some of the VOCs (de Percin, 1991c).

High molecular weight organic compounds may foul or plug baghouses or condenser systems, therefore, the types of petroleum products that may be treated by specific technologies may be limited. Rotary dryers typically can treat soils that have an organic content of less than two percent. Thermal screw units may treat soils that contain up to 50% organics. (Troxler, personal communication, 1991).

Thermal desorption has several advantages over other treatment processes. It treats a wide range of organic contaminants, is mobile, commercially available, and enjoys more public acceptance than other thermal treatment methods (de Percin, 1991a). Also, because thermal desorbers operate at lower temperatures than incinerators, significant fuel savings may result (Vatavuk, 1990). They also produce smaller volumes of off-gases to treat than incinerators. Thermal desorption also differs from incineration in the regulatory and permitting requirements and in the partitioning of metals within the process residual streams.

Potential limitations of the treatment process exist as well. Foremost, thermal desorption does not destroy contaminants; it merely strips them from the solid or liquid phase and transfers them to the gas-phase. Therefore, devices to control VOC emissions are necessary. Since metals (e.g., Pb) tend to remain in the soil after treatment, further treatment of the soil, such as stabilization, may be required. The efficiency of the thermal desorption process will vary with the chemical and physical properties of the specific contaminants.

A generalized schematic diagram of a thermal screw, thermal desorption process is shown in Figure 4-2; the system shown most closely resembles Weston's LT^3 system. Other designs may use different types of control technology. Information about specific vendor designs is given below. The information in this section is primarily based upon the use of portable remediation units, but the information should also be generally applicable to other types of thermal desorption such as rotary drum aggregate dryers.

X*TRAX™ by Chemical Waste Management, Inc.

A transportable, indirectly heated rotary dryer, the X*TRAX™ system treats up to 100 tons of soil and sediment contaminated with hazardous wastes per day. Propane fires an outer shell which then heats the soil to 300°-900°F. Nitrogen gas sweeps the water and organic vapor to gas treatment and mitigates explosion hazards. Gas treatment comprises condensation, refrigeration, and carbon adsorption. The liquid water is separated from the liquid organic compounds and used for dust control (de Percin, 1991b).

Taciuk by SoilTech, Inc.

The Taciuk system is a two-zone, double-shell rotary dryer that treats up to 25 tons of soil and sediments contaminated with hazardous wastes per hour. The solids enter the first zone of the inside shell where temperatures of 300°F vaporize water and volatile organic compounds (VOCs). Entry into the second zone of the inside shell enables additional organic compounds to be volatilized and pyrolyzed at temperatures of 1000°F. These high temperature solids enter the outer shell where they transfer heat to the inner shell. Fired natural gas or propane heats the annulus between the shells. A cyclone, baghouse, caustic scrubber, and carbon adsorber treat the combustion gases while a condenser liquifies gases from both zones. Non-condensable gases from pyrolysis help to heat the system (de Percin, 1991b).

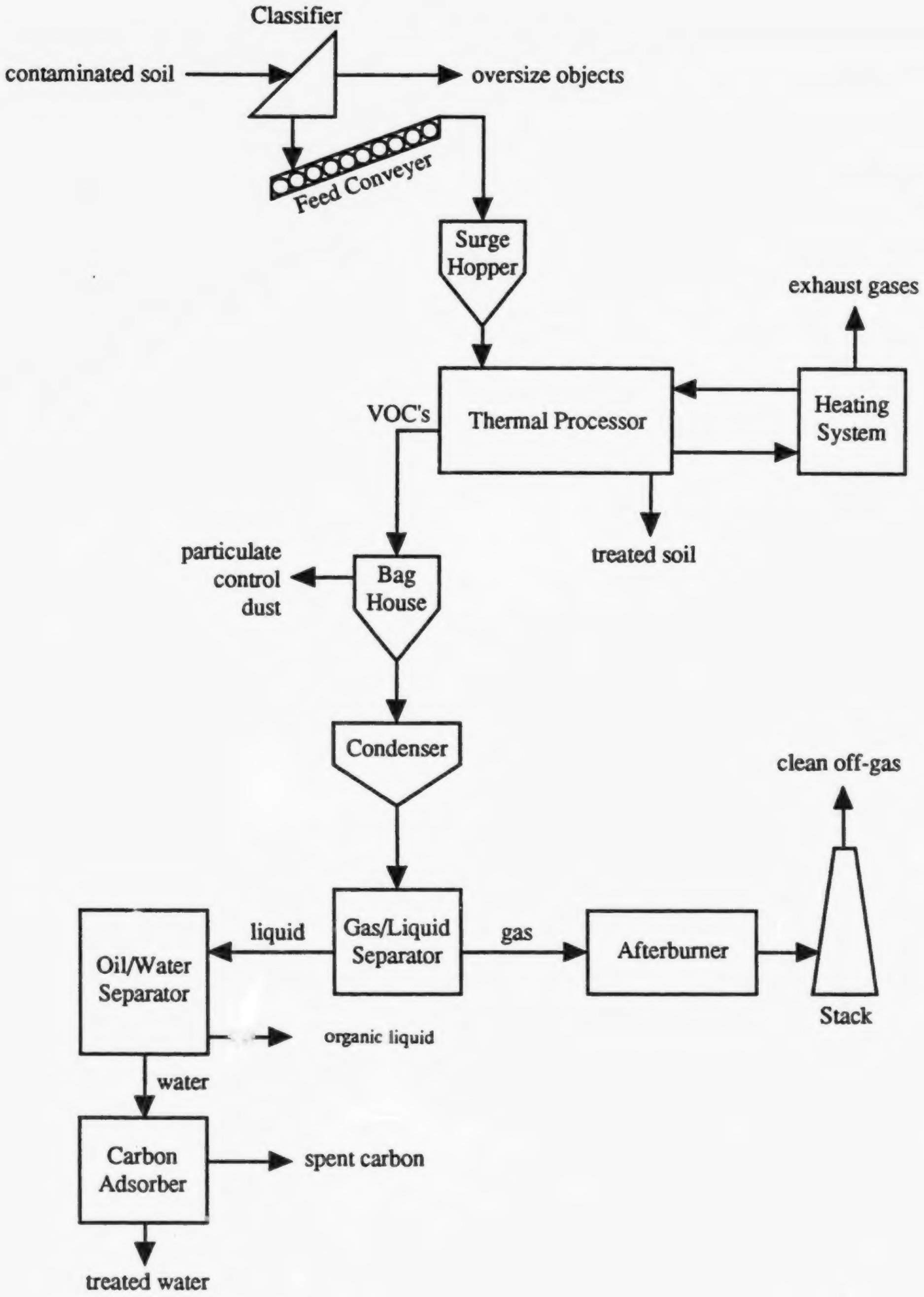
Classifier
contaminated soil
oversize objects
Feed Conveyer
Surge Hopper
exhaust gases
VOC's
Thermal Processor
Heating System
treated soil
particulate control dust
Bag House
Condenser
clean off-gas
liquid
Gas/Liquid Separator
gas
Afterburner
Oil/Water Separator
Stack
organic liquid
water
Carbon Adsorber
spent carbon
treated water

Figure 4-2. Generalized Process Diagram for Thermal Screw-Based Thermal Desorption.

LT^3 by Roy F. Weston, Inc.

The Low Temperature Thermal Treatment, or LT^3 system, treats up to 20 tons of soil and sediment per hour using two banks of four heated screws. The process is used primarily for treating hazardous wastes. The combustion of propane heats transfer oil, which is pumped through the screws, heating the shell to 600°F. The combustion gases sweep the water and organic vapor to the gas treatment system (de Percin, 1991b).

DAVES by Recycling Sciences, Inc.

The Desorption and Vapor Extraction System (DAVES) treats contaminated material in a fluidized bed where it is fed along with hot air. Gas-fired heaters heat the air to 1000°-1400°F. The hot air vaporizes water and organic compounds and carries them to the gas treatment system. Gas treatment consists of a cyclone, baghouse, venturi scrubber, chiller, and carbon adsorber (de Percin, 1991b).

ReTec by Remediation Technologies, Inc.

The ReTec thermal desorption system operates at capacities of 0.5 - 3.5 tons/hr and is designed to treat soils contaminated with organic compounds and oily sludges. The process begins with a dewatering step if the waste material has a high moisture content. Dewatered filter cakes from the press are fed to storage hoppers and then transported to the dryer by a covered conveyer. The Holo-Flite® Processor consists of a jacketed trough which houses a double-screw mechanism. The heat transfer fluid is circulated through the trough jacket can by thermal oil or steam. The material enters and exits the dryer through rotary air-locks to prevent leakage of ambient air into the processor. The gas flow from the dryer, which is designed to remove moisture and lower boiling organic compounds, passes through a particle removal system, quench chamber, condenser and activated carbon beds (Abrishamian, 1991).

The partially treated soil leaves the dryer and enters the processor where the soil is subjected to temperatures up to 900°F and shorter residence times (relative to the drying step) to remove higher boiling organic compounds. Heated by an electric or fuel-fired heater, molten salt is used as the heating medium for the processor. Molten salt operates at temperatures between 500° and 950°F, does not produce off-gases, and has the additional advantages of being non-toxic, non-flammable, and easily cleaned up if spilled. Inert gas added to the processor inhibits oxidation and enhances vaporization of contaminants. Off-gases from the processor undergo treatment with cyclones, a semi-volatile organic separator, chilled condenser, and activated carbon beds. A solids cooler lowers the temperature of the solids to less than 180°F for safe handling (Abrishamian, 1991).

4.2 Identification of Air Emission Points

The air emissions associated with thermal desorption come from several sources. Most studies include data about contaminant concentrations in the soil directly before and after treatment, which can yield information about point source air emissions from the desorption process itself. These studies do not address, however, the change in concentration before and after excavation due to volatilization. Similarly, little data is available on fugitive emissions from individual units in the process other than the desorption chamber and from the other waste streams.

Point sources of air emissions from thermal desorption vary widely with each process. The stack of an afterburner vents combustion products, as does a fuel-fired heating system if the combustion gases are not fed into the desorber. The fuel-fired heating system typically operates with propane, natural gas or fuel oil. If VOC emission controls consist of a baghouse, scrubber, and vapor phase carbon adsorber, the stack will vent small concentrations of the original contaminants, as well as products of any chemical reactions that might occur.

The volume of off-gas from a thermal desorption unit depends on the type of processor. Devices that are heated indirectly have off-gases composed of volatilized VOCs and water from the soil being treated and possible some sweep gas used to carry the contaminants out of the device. This volume of gas is typically 1000 to 5000 acfm (Troxler, personal communication, 1991). In directly heated units, the off-gas contains volatilized contaminants and water, but also the combustion gases used to heat the soil. The result is a much larger volume of off-gas that needs to be treated, around 10,000 to 50,000 acfm (Troxler, personal communication, 1991). Therefore, off-gases from indirectly heated LTTDs, i.e. thermal screws, can be treated with smaller chemical/ physical systems, such as a baghouse, a condenser, and then an afterburner.

Fugitive emissions from area sources may contribute significantly to the total air emissions from a remediation site. Probably the largest source is excavation of the contaminated soil. Other sources may include the classifier, feed conveyor, and the feed hopper. Fugitive emissions from the components of the thermal desorption system and controls are possible as well. Emissions may also emanate from the waste streams such as exhaust gases from the heating system, treated soil, particulate control dust, untreated oil from the oil/water separator, spent carbon from liquid or vapor phase carbon adsorber, treated water, and scrubber sludge.

4.3 Typical Air Emission Species of Concern

The volatile and semi-volative contaminants under remediation are the species emitted if no destruction or other chemical treatment has taken place. The sources emitting these VOCs may include excavation, soil handling, classifier, oversize objects rejected by the classifier, feed conveyor, feed hopper, control stack, and fugitive emissions from the entire thermal desorption system and from waste streams. Combustion products are emitted when a destructive control device such as an afterburner is used and also when the heating system is fuel-fired. In some cases, pyrolysis occurs to a certain degree in the dryer, so products from these reactions may also be emitted.

4.4 Summary of Air Emissions Data

There is little published data of the levels of air emissions from thermal desorption systems. This reflects the relatively early stage of commercial development for this technology.

4.4.1 Air Emissions Data for Asphalt Aggregate Dryers

The VOC emissions from asphalt aggregate dryers will vary by several orders of magnitude depending on whether afterburners are used as a control device.

Soil Purification, Inc. (SPI), a subsidiary of a leading manufacturer of asphalt plants, has estimated the typical emissions for soil treatment in a modified asphalt aggregate dryer. This system consists of a direct-fired rotary drum operating at 550-1000°F. A primary cyclonic tube collector and pulse-jet baghouse are used to control particulate emissions. A thermal oxidizer (i.e., afterburner) destroys organic compounds in the off-gas stream (99-99.99% efficiency). Based on a processing rate of 35-60 tons per hour, typical emissions from this type of unit are:

- Particulate - 0.02-0.03 gr/dscf; and
- Total VOC - 0.1-5 lb/hr.

Data were identified for three asphalt plants that were modified for the treatment of petroleum contaminated soils. Afterburners were not used on any of these systems. A summary of the data is presented in Table 4-2. Each site will be discussed in more detail below.

Soil contaminated with diesel fuel and gasoline were treated at an asphalt plant with a 450 tons/hour capacity at 5% moisture (Barr, 1990). Soil enters the dryer opposite of the burner and flows countercurrent to the combustion gases. This configuration allows the VOCs which desorb from the soil in the upper portion of the dryer to exit the system without exposure to the burner flame. The results presented for this plant, labelled Barr, represent the worst case conditions since all of the VOCs

Table 4-2.
Summary Data for Asphalt Kilns

Site	Process Parameter	Value, Units	Contaminant	Soil Characteristics			Off-gas Characteristics		
				Initial Concentration (ppm)	Final Concentration (ppm)	Removal Efficiency	Stack Concentration	Units	Estimated Emission Rate (g/hr)
1. Barr Engineering (Barr, 1990)									
Diesel Contaminated Soil									
	Processing Equipment	Asphalt Plant	Benzene	19.5	<.01	99.9	4.3	ppm,d	15
	Control Equipment	Wet scrubber	Toluene	<.5	0.1		0.6	ppm,d	2.4
		Cyclonic demister	Xylenes-m,p	<.8	0.2	93.2-99.9	0.42	ppm,d	1.92
	Air Flow	80,000 acfm at 300°F	xylene-o	3.1	<.01	93.2-99.9			
	Feed Rate	280 tons/hr	THC				2590	ppm	115200
	Stack Exit Gas Temperature	150°F	Naphthalene				6757	ug/Nm3	7.80096
			Acenaphtylene				901	ug/Nm3	1.03824
			Acenaphthene				638	ug/Nm3	0.73782
			Fluorene				763	ug/Nm3	0.90876
			Phenanthrene				645	ug/Nm3	0.74268
			Anthracene				427	ug/Nm3	0.49032
			Fluoranthene				135	ug/Nm3	0.15546
			Pyrene				111	ug/Nm3	0.12744
			Benzo(a)anthracene				<=9	ug/Nm3	0.01008
			chrysene				7.5	ug/Nm3	0.00282
			benzo(b)fluoranthene				<=4.9	ug/Nm3	0.00558
			benzo(k)fluoranthene				<=9	ug/Nm3	0.01008
			benzo(a)pyrene				<=2.0	ug/Nm3	0.00228
			indeno(1,2,3-c,d)pyrene				<=4.5	ug/Nm3	0.00504
			dibenzo(a,h)anthracene				<=4.4	ug/Nm3	0.00492
			benzo(g,h,i)perylene				<=6.0	ug/Nm3	0.00672
			Particulate				0.2	gr/dscf	29000
Gasoline Contaminated Soil									
	Processing Equipment	Asphalt Plant	Benzene	39.5	<.01	99.9	8.6	ppm,d	30.6
	Control Equipment	Wet scrubber	Toluene	<2	<.02		0.8	ppm,d	3.36
		Cyclonic demister	Xylenes-m,p	<3	1.2	93.2-99.9	3.5	ppm,d	16.8
	Air Flow	80,000 acfm at 300°F	xylene-o	15.6	<.01	93.2-99.9			
	Feed Rate	280 tons/hr	THC				2800	ppm	140600
	Stack Exit Gas Temperature	150°F	Naphthalene				5136	ug/Nm3	5.5644
			Acenaphtylene				634	ug/Nm3	0.68784
			Acenaphthene				317	ug/Nm3	0.35628
			Fluorene				405	ug/Nm3	0.46206

Table 4-2. (Continued)

Site	Process Parameter	Value, Units	Contaminant	Soil Characteristics			Off-gas Characteristics		
				Initial Concentration (ppm)	Final Concentration (ppm)	Removal Efficiency	Stack Concentration	Units	Estimated Emission Rate (g/hr)
			Phenanthrene				385	ug/Nm3	0.43656
			Anthracene				<1.4	ug/Nm3	0.00162
			Fluoranthene				24	ug/Nm3	0.02682
			Pyrene				32	ug/Nm3	0.03474
			Benzo(a)anthracene				<4	ug/Nm3	0.0045
			chrysene				<.8	ug/Nm3	0.0009
			benzo(b)fluoranthene				<2.2	ug/Nm3	0.00252
			benzo(k)fluoranthene				<3.9	ug/Nm3	0.00444
			benzo(a)pyrene				<.9	ug/Nm3	0.00096
			indeno(1,2,3-c,d)pyrene				<2	ug/Nm3	0.00222
			dibenzo(a,h)anthracene				<2	ug/Nm3	0.00222
			benzo(g,h,i)perylene				<2.6	ug/Nm3	0.003
			Particulate				0.2	gr/dscf	30400
			Petroleum Hydrocarbons			85-94			
2. Petroleum Contaminated Soil (Batten, 1987)									
	Processing Equipment	rotary drum dryer	Benzene	0.11	0.06	84.5			
	Control Equipment	baghouse	Toluene	0.27	<.01	100			
	Feed Rate	120 tons/hr	Xylenes	13.1	0.1	100			
	Soil Temperature	350-400F	ethylbenzene	0.11	<.01	100			
	Residence Time	2-3 min	total petroleum HC	440	<=5.5	97			
			THC	39-393	5.7-9.5	61-65	129-175	ppmv as propane	
3. Soil Cleanup System at Kingvale (SCS, 1990)									
	Processing Equipment	rotary kiln, asphalt plant	non-methane VOCs			89	268	ppmv	472
	Manufacturer	Earth Purification Engineering, Inc.	Semi-VOAs						712
	Control Equipment	cyclones	VOCs+Semi-VOAs			71			
		baghouse	Particulate				0.1278	gr/dscf	
	Feed Rate	1.8 yd3/hr	Diesel	1875	<1				
	Soil Temperature	775F							
	Exit Gas Temperature	800-1000F							
	Estimated Diesel Input	9.1 lb/hr							
	Exhaust Gas Flow	1552 dscfm							
	Soil Processed	150 yd3							

volatilized from the soil may not be destroyed and no additional VOC control device is present (Barr, 1990). The hot exhaust gases are routed to a wet scrubber and a cyclonic demister. The gas is then emitted to the atmosphere through the stack.

The feed rate for the diesel fuel and gasoline contaminated soils for the test runs were 280 and 255 tons/hour, respectively. The air pollution control equipment accommodates 80,000 acfm at 300°F (Barr, 1990). The soil headspace concentrations and removal efficiencies are reported for the remediation tests. The uncontrolled organic and controlled particulate emissions are also presented in Table 4-2. Measured total hydrocarbon (THC) emission rates for these tests were 254 to 310 lb carbon per hour (i.e., about ten times the typical emission rate during asphalt production). Emission rates of particulate matter were 64 to 67 lbs/hour.

A second trial burn was performed on a soil contaminated with petroleum hydrocarbons. The plant treats up to 120 tons/hour of soil at temperatures around 350-400°F (Batten, 1987). The soil concentrations, removal efficiencies and emissions data are presented in Table 4-2 for VOCs and other components. The exhaust gas from the system contained 129 to 175 ppmv of THC above background. THCs were emitted at a rate between 30.4 and 47.7 lb/hr. The estimated emission factor for total non-methane hydrocarbons was 0.21 to 0.26 lbs per ton of soil treated. Based on the results, Batten (1987) concluded that hydrocarbon controls would be necessary in order for the asphalt kiln to meet air pollution control requirements.

The Soil Cleanup System (SCS, from Earth Purification Engineering Inc.) was demonstrated in the treatment of a diesel contaminated soil from a leaking underground fuel tank in Kingvale, California. The SCS is an asphalt recycling unit modified to treat contaminated soils. The offgas from the rotary kiln is routed to dual cyclones, an exhaust cooler, and a baghouse. The soil exits the system at 775°F. The results for this site are presented in Table 4-2. The emission rates for non-methane VOCs and semi-volatile organics were 1.04 and 1.57 lb/hour, respectively, or 0.44 and 0.67 lb/ton assuming 1.25 ton/yd^3 (SCS, 1990).

4.4.2 Air Emissions Data for Mobile Units

Several sets of data were found for the treatment of various contaminated soils by thermal desorption. Table 4-3 presents a summary of the data for all of the sites. The data represent the treatment of soils contaminated with petroleum fuels and soils contaminated with hazardous wastes. Each set of data is described in more detail below.

According to Weston Services, Inc., the use of their full-scale LT^3 system on the Springfield, Illinois cleanup of gasoline and No. 2 fuel oil contaminated soils produced stack emissions that were in compliance with federal and state regulations, including VOCs, HCl, CO, and particulates (Nielson and Cosmos, 1989). The emission rate of BTEX (benzene, toluene, ethylbenzene, and xylene) was 1055 grams/hour before controls and 21 grams/hour after the control devices, as shown in Table 4-3.

ReTec's thermal adsorption unit was used in the remediation of a coal tar contaminated soil. Molten salt in a thermal screw was used to indirectly heat the soil to approximately 450°F. The soil was treated at a rate of 100 pounds per hour. The controlled emissions of BTEX were 0.26 grams per hour or 0.011 lb/ton (U.S. EPA, 1991). Initial and final soil concentrations for various contaminants are also presented in Table 4-3.

At the McKin Superfund Site in Gray, Maine, soil containing primarily trichloroethylene (TCE) was treated by Canonie Environmental Services Corporation. Temperatures varied between 150 and 380°F, and the capacity was 1-4 cubic yards per batch. To achieve 0.1 ppm TCE concentration in the treated soil, the temperature was adjusted to 300°F for 6-8 minutes (Webster, 1986). The concentration reductions, removal efficiencies, and emission rates for VOCs are presented in Table 4-3. The total reported emission rates were 24 g/hr.

Table 4-3.
Summary Data for Mobile Thermal Desorption Units

Site	Process Parameter	Value, Units	Contaminant	Soil Characteristics				Offgas Characteristics				
				Initial Concentration	Final Concentration	Units	Removal Efficiency	Control Efficiency	Stack Concentration	Units	Uncontrolled Emission Rate (g/hr)	Estimated Controlled Emission Rate (g/hr)
1. LT3 full scale on no.2 fuel oil and gasoline contaminated soils (Nielson and Cosmos, 1991; U.S. EPA, 1991)												
	Processing Equipment	Thermal screw	benzene	1000	5.2	ppb	99.5	98			163	3.27
	Manufacturer	Weston Services Inc.										
	Heating Medium	Oil	toluene	24000	5.2	ppb	99.9	98			749	15
	Control Equipment	Fabric Filter	xylene	110000	<1	ppb	>99.9	98			136	2.72
		Condenser	ethylbenzene	[illegible]000	4.8	ppb	99.9	98			31.1	0.622
		Afterburner	naphthalene	4900	<330	ppb	>99.3	98				
	Feed Rate	7.5 tons/hr	Carcinogenic Priority PNAs									
	Soil Temperature	350-400F	benz(a)anthracene	<6000	<330	ppb	<94.5					
	Residence Time	70 min	benzo(a)pyrene	<6000	<330	ppb	<94.5					
			benzo(b)fluoranthene	<6000	<330	ppb	<94.5					
			chrysene	<6000	590	ppb	<90.2					
			dibenzo(ah)anthracene	<6000	<330	ppb	<94.5					
			Noncarcinogenic Priority PNAs									
			acenaphthene	890	<330	ppb	>62.9					
			acenaphthalene	1200	<330	ppb	>72.5					
			anthracene	2700	<330	ppb	>87.8					
			benzo(ghi)perylene	<6000	<330	ppb	<94.5					
			benzo(k)fluoranthene	<6000	<330	ppb	<94.5					
			fluoranthene	<6000	<330	ppb	<94.5					
			fluorene	4900	<330	ppb	<93.3					
			indeno(123-cd)pyrene	<6000	<330	ppb	<94.5					
			phenanthrene	2400	430	ppb	82.1					
			pyrene	<6000	<330	ppb	<94.5					
2. ReTec's Pilot Unit with Coal tar contaminated soils (U.S. EPA, 1991)												
			benzene	1.7	<.1	ppm	>94	95			0.726	0.0363
	Processing Equipment	Thermal Screw	toluene	2.3	<.1	ppm	>95	95			0.999	0.0499
	Heating Medium	molten salt	ethylbenzene	1.6	<.1	ppm	>93	95			0.681	0.034
	Control Equipment	cyclones	xylenes	6.3	<.3	ppm	>95	95			2.72	0.136
		semi-voa separator	naphthalene	367	<1.7	ppm	>99	95			166	8.29
		chilled condenser	fluorene	114	<.2	ppm	>99					
		activated carbon beds	phenanthrene	223	18	ppm	91.9					
	Feed Rate	100 lb/hr	anthracene	112	7	ppm	93.8					

Table 4-3. (Continued)

Site	Process Parameter	Value, Units	Contaminant	Soil Characteristics				Offgas Characteristics				
				Initial Concentration	Final Concentration	Units	Removal Efficiency	Control Efficiency	Stack Concentration	Units	Uncontrolled Emission Rate (g/hr)	Estimated Controlled Emission Rate (g/hr)
	Treatment Temperature	450F	fluoranthene	214	15	ppm	93					
			pyrene	110	11	ppm	90					
			benzo(b)anthracene	56	<1.4	ppm	>97					
			chrysene	58	3.7	ppm	93.6					
			benzo(b)fluoranthene	45	<1.4	ppm	>97					
			benzo(k)fluoranthene	35	<2.1	ppm	>94					
			benzo(a)pyrene	47	<.9	ppm	>98					
			benzo(ghi)perylene	24	<1.1	ppm	>95					
			indeno(123-cd)pyrene	27	<6.2	ppm	>77					
3. McKin Superfund Site, TCE contaminated soil (Webster, 1986)												
	Manufacturer	Canonie Environmental Services Corp.	Trichloroethylene	17-115	nd, 0.05	ppm	>99	95			220	11
	Control Equipment	baghouse	tetrachloroethylene	11-19	nd, 0.05	ppm	>99	95			36.2	1.81
		packed tower air scrubber	1,1,1-trichloroethane	.11-.3	nd, 0.05	ppm	>55	95			0.478	0.0239
		carbon bed adsorbers	1,2-dichlorobenzene	3.5-50	nd, 1	ppm	>71	95			93.7	4.68
	Residence time	6-8 min	toluene	1-2	nd, 1	ppm	>0	95			19.91	0.0956
	Soil temperature	300F	xylenes	5-69	nd, 1	ppm	>80	95			130	6.5
	Feed Rate	4212 lb/hr										
4. Thermotech Systems Corporation (Thermotech, 1990-1991)												
	Control Equipment	dust collector										
		thermal oxidizer										
	Air Flow	64,000 acfm										
	Afterburner Retention Time	2 sec										
	DRE	95-98%										
Washington, D.C.												
	Afterburner Temperature	1408F	particulate						0.0077	gr/acf		
	Flow Rate	39014 acfm; 7484 dscfm							0.038	gr/dscf		2.38
			benzene						0.79	ppm		0.102
			toluene						<=.12	ppm		<=.0187
			ethylbenzene						<=.03	ppm		<=.0041
			xylene						<=.05	ppm		<=.0077
			TPH						21.7	ppm		0.42

Table 4-3. (Continued)

Site	Process Parameter	Value, Units	Contaminant	Soil Characteristics				Offgas Characteristics				
				Initial Concentration	Final Concentration	Units	Removal Efficiency	Control Efficiency	Stack Concentration	Units	Uncontrolled Emission Rate (g/hr)	Estimated Controlled Emission Rate (g/hr)
Grand Rapids, MN			Particulate						0.0131	gr/acf		
	Feed Rate	33.8 tons/hr							0.064	gr/dscf		4.98
	Afterburner Temperature	1445F										
	Flow Rate	51366 acfm; 9070 dscfm										
5. Mobile Thermal Processor, Model 100 (Remedial Technology Unit, 1990)												
	Manufacturer	U.S. Waste Thermal Proc.										
	Control Equipment	Venturi scrubber										
		Afterburner										
Gasoline Contaminated Soil												
	Feed Rate	5.65 yd3/hr	Particulates						0.0084	gr/dscf		4.2
	Moisture	7.23%	Gasoline	5000	nd	mg/kg						
	Soil Exit Temperature	299F	Dioxins						nd	ug/dscm		
	Afterburner Temperature	1825F	Furans						nd	ug/dscm		
	Flow Rate	2491 dscfm	Dichlorobiphenyl						0.073	ug/dscm		
			other PCBs						nd	ug/dscm		
			naphthalene						nc	ug/dscm		
			phenanthrene						33	ug/dscm		
			anthacene						1.5	ug/dscm		
			fluoranthene						1.3	ug/dscm		
			pyrene						1.7	ug/dscm		
			other PAHs						nd	ug/dscm		
Diesel Contaminated Soil												
			Particulates						0.0057	gr/dscf		2.7
	Feed Rate	3.95 yd3/hr	Diesel	5500	nd	mg/kg						
	Moisture	6.34%	Dioxins						nd	ug/dscm		
	Soil Exit Temperature	450F	Furans						nd	ug/dscm		
	Afterburner Temperature	1825F	Dichlorobiphenyl						nd	ug/dscm		
	Flow Rate	2361 dscfm	other PCBs						nd	ug/dscm		
			naphthalene						6.6	ug/dscm		
			phenanthrene						13	ug/dscm		
			anthacene						0.25	ug/dscm		
			fluoranthene						nd	ug/dscm		
			pyrene						nd	ug/dscm		
			other PAHs						nd	ug/dscm		

Table 4-3. (Continued)

Site	Process Parameter	Value, Units	Contaminant	Soil Characteristics				Offgas Characteristics				
				Initial Concentration	Final Concentration	Units	Removal Efficiency	Control Efficiency	Stack Concentration	Units	Uncontrolled Emission Rate (g/hr)	Estimated Controlled Emission Rate (g/hr)
6. Todds Lane Soil Remediation Plant (United Engineers and Constructors, 1991)												
	Control Equipment	cyclone	benzene (max,avg)					99	20,3.7	ppm		0.0696
		multiclones	toluene (max,avg)					99	100,24	ppm		0.348
		baghouse	ethylbenzene (max,avg)					99	360,69	ppm		1.25
		afterburner	xylene (max,avg)					99	130,35	ppm		0.452
	Feed Rate	185 tons/hr										
	Afterburner Efficiency	99%										
7. Soil Remediation Unit 202 (Air Consulting and Engineering, 1991)												
	Processing Equipment	portable rotary kiln	VOC				88.3	99	13.6	ppm dry as propane		0.74
	Control Equipment	afterburner					95.4	99	6.3	ppm dry as propane		0.29
		baghouse					98.4	99	2.5	ppm dry as propane		0.1
	Feed Rate	25 tons/hr	Particulate					95	0.0303	gr/scf		2.52
	Afterburner Temperature	1400F						95	0.0266	gr/scf		1.89
	Afterburner Retention Time	.5 sec						95	0.076	gr/scf		1.65
	Stack Flow Rate	8300 scfmd										
8. X*TRAX pilot scale (U.S. EPA, 1991)												
	Processing Equipment	externally fired rotary kiln										
	Control Equipment	wet scrubber										
		condenser										
		particulate filter										
		carbon adsorption unit										
		secondary scrubber										
	Feed Rate	4.5 metric tons/hr at 30% moisture										
		Clay	PCBs	5000	24	ppm	99.3		<.00056	mg/m3		
			VOCs	1320	57	ppmv	95.6					0.02
		Silty clay	PCBs	2800	19	ppm	99.5		<.00055	mg/m3		
			VOCs	1031	72	ppmv	93					0.03
		clay	PCBs	1600	4.8	ppm	99.7		<.00051	mg/m3		
			VOCs	530	35	ppmv	93.3					0.01
		sandy	PCBs	1480	8.7	ppm	99.1		<.00058	mg/m3		
			VOCs	2950	170	ppmv	94.2					0.07
		clay	PCBs	630	17	ppm	97.3		<.00052	mg/m3		
			VOCs	2100	180	ppmv	91.4					0.08

Table 4-3. (Continued)

Site	Process Parameter	Value, Units	Contaminant	Soil Characteristics				Offgas Characteristics				
				Initial Concentration	Final Concentration	Units	Removal Efficiency	Control Efficiency	Stack Concentration	Units	Uncontrolled Emission Rate (g/hr)	Estimated Controlled Emission Rate (g/hr)
9. IT Corporation, Burlington Northern Site (IT, 1991)												
	Processing Equipment	rotary dryer with nitrogen	phenol	<2.3	<.043	mg/kg	na		46600	ug/m3		
	Control Equipment	scrubber	2-methylphenol	<1.3	<.023	mg/kg	na		7700	ug/m3		
		condenser	4-methylphenol	<1.9	<.033	mg/kg	na		20300	ug/m3		
		HEPA filter	2,4-dimethylphenol	<6.6	<.12	mg/kg	na		4800	ug/m3		
		activated carbon unit	naphthalene	130	<.016	mg/kg	>99.99		138000	ug/m3		
		secondary scrubber	2-methylnaphthalene	170	<.19	mg/kg	>99.89		165000	ug/m3		
	Soil Temperature	1025F	acenaphthylene	36	<.007	mg/kg	>99.98		87000	ug/m3		
	Residence Time	10 min	acenaphthene	320	<.21	mg/kg	>99.93		327000	ug/m3		
	Moisture	4.64-6.87%	dibenzofuran	220	<.081	mg/kg	>99.96		266000	ug/m3		
			fluorene	365	<.02	mg/kg	>99.9		512000	ug/m3		
			phenanthrene	965	<.034	mg/kg	100		1600000	ug/m3		
			anthracene	390	<.073	mg/kg	>99.98		770000	ug/m3		
			fluorantheme	630	<.01	mg/kg	100		1040000	ug/m3		
			pyrene	550	<.052	mg/kg	>99.99		770000	ug/m3		
			benzo(a)anthracene	160	<.023	mg/kg	>99.98		255000	ug/m3		
			chrysene	890	<.12	mg/kg	>99.92		325000	ug/m3		
			bis(2-ethylhexyl)phthalate						2100	ug/m3		
			benzo(b) and (k)fluoranthene	150	<.047	mg/kg	>99.97		276000	ug/m3		
			benzo(a)pyrene	72	<.11	mg/kg	>99.84		104000	ug/m3		
			indeno(123-cd)pyrene	<=24	<.035	mg/kg	na		39000	ug/m3		
			dibenzo(ah)anthracene	<=3.8	<.016	mg/kg	na		20500	ug/m3		
			benzo(ghi)perylene	<=24	<.32	mg/kg	na		32500	ug/m3		
			Mercury	18	0.77	mg/kg	95.04					
			methylene chloride	BDL					5000	ug/m3		
			acetone	BDL								
			carbon disulfide	BDL								
			2-butanone	nd					27000	ug/m3		
			1,1,1-trichloroethane	nd								
			trichlorotrifluoroethane	BDL								
			benzene	BDL					410000	ug/m3		
			toluene	BDL					450000	ug/m3		
			xylenes	BDL					220000	ug/m3		
			trichlorofluoromethane	BDL								

Table 4-3. (Continued)

Site	Process Parameter	Value, Units	Contaminant	Soil Characteristics				Offgas Characteristics				
				Initial Concentration	Final Concentration	Units	Removal Efficiency	Control Efficiency	Stack Concentration	Units	Uncontrolled Emission Rate (g/hr)	Estimated Controlled Emission Rate (g/hr)
			chloromethane						11000	ug/m3		
			1,1-dichloroethane						650	ug/m3		
			1,1-dichloroethane						700	ug/m3		
			chloroform						930	ug/m3		
			bromodichloromethane						450	ug/m3		
			trichloroethene						400	ug/m3		
			ethylbenzene						47000	ug/m3		
			styrene						67000	ug/m3		

The Thermotech Systems Corporation's Portable Soil Remediation Unit was used to treat petroleum contaminated soils in Washington, D.C. and Grand Rapids, MN. The unit has air pollution controls for particulate matter (dust collector) and organics (thermal oxidizer). The average particulate and VOC emissions of three runs are presented in Table 4-3. For the Washington, D.C. site, the particulate, BTEX, and TPH emissions were 5, less than or equal to 0.13, and 0.42 pounds per hour, respectively. The emission rate for particulates from the Grand Rapids site were 2.4 lb/hr (Thermotech, 1990-1991).

U.S. Waste Thermal Processing's Mobile Thermal Processor, Model 100, was used to treat gasoline and diesel contaminated soils. The transportable treatment unit consists of a primary furnace with an afterburner to incinerate the combustibles. The offgas from the afterburner is routed to a wet scrubber for particulate removal. The soil exit temperature is maintained between 300 and 650°F, and the afterburner operates at 1800°F, with a minimum residence time of 0.5 seconds. The scrubber is a dual-venturi collision scrubber. The test was performed on soil at 5000 and 5500 mg/kg contamination levels of gasoline and diesel fuel, respectively. The particulate emission rates were 4.2 and 2.7 lb/day (Remedial Technology Unit, 1990).

The Todds Lane Soil Remediation Plant handles soils contaminated with petroleum hydrocarbons. Pollution control devices include a cyclone, multiclones, a baghouse, and an afterburner. The maximum anticipated concentrations of certain VOCs in the soil were used to estimate the emission rates of the compounds after the afterburner, assuming 99% efficiency. The total emission rate for BTEX was determined to be 2.1 pounds per hour (United Engineers and Constructors, 1991).

The Soil Remediation Unit (SRU) 202 consists of a rotary kiln, an afterburner and a baghouse. This unit was used to treat contaminated soil, and the emissions were reported as follows: particulate - 1.7 to 2.5 lb/hr and VOC - 0.1 to 0.74 lb/hr (Air Consulting and Engineering, 1991).

The pilot-scale X*TRAX system uses an externally fired rotary kiln for the treatment of soils contaminated with hazardous wastes. The offgas is first treated in a liquid scrubber where particulate matter is removed. The gas is then cooled further to allow for condensation of the contaminants. The gas is routed through a particulate filter and to a carbon adsorber where most of the remaining organics are removed. The VOC emissions ranged from 0.01-0.08 lb/day for the treatment of clay and sandy soils (U.S. EPA, 1991).

A pilot-scale test was performed by IT Corporation for the treatment of creosote contaminated soils at the Burlington Northern Superfund Site. The thermal desorption unit was operated at 1025°F and a residence time of 10 minutes. The LTTD unit consists of a rotating desorber tube partially enclosed within a gas-fired furnace shell. Nitrogen is introduced into the system to flush out desorbed contaminants and to maintain an atmosphere that does not support combustion. The offgas is treated with a cyclone, a primary scrubber, a condenser, a demisting filter, a particulate filter and an activated carbon unit. Finally, the offgas is scrubbed in a secondary scrubber and then discharged to the atmosphere. Pretreatment and post-treatment soil analyses are presented in Table 4-3 for VOCs and semi-volatile organics. The removal efficiencies and stack gas concentrations are also presented. These values represent the average of six samples (IT, 1991). The IT system was also used to treat PCB contaminated soils at a rate of 40 to 70 pounds per hour. The result of these tests are presented separately in Table 4-4; the operating temperature and residence time varied for each run.

4.5 Identification of Applicable Control Technologies

Control of volatile organic emissions is crucial to the overall success of thermal desorption remediation of contaminated soils. Because the process uses physical separation driven by heat, the vaporized contaminants would simply be transferred from one medium (soil) to another (air) if no emission controls were employed. The types of controls include both destruction and separation technologies. Typically two to six

Table 4-4.

Estimated Emissions of Selected Compounds for the Cleanup of PCB-Contaminated Soil using the IT Process

Contaminant	Residence Time (minutes)	Temperature °F	Initial Concentration	Final Concentration	Units	Rate of Uncontrolled Emissions g/hr	Overall Estimated Percent Efficiency	Estimated Emissions Rate g/hr
PCB's	19	1022	37.5	2	ppm	1.14	95%	5.68e-02
2,3,7,8-TCDD	40	1040	260	0.018	ppb	0.00832	95%	4.16e-04
2,3,7,8-TCDD	19	1040	236	0.018	ppb	0.00755	95%	3.78e-04
2,3,7,8-TCDD	10.5	1040	266	0.018	ppb	0.00851	95%	4.26e-04
2,3,7,8-TCDD	24	860	233	0.5	ppb	0.00744	95%	3.72e-04
2,3,7,8-TCDD	5.6	1022	48	0.084	ppb	0.00153	95%	7.67e-05
2,3,7,8-TCDD	20	1031	56	0.23	ppb	0.00178	95%	8.92e-05

controls in series are chosen to suit the specific VOC contaminants present and the other pollutants of concern. Liquid phase and solid waste streams are usually treated on site or stored for subsequent off-site treatment. Typical VOC controls for point sources are briefly described below; Section 5.5 contains additional information. More detailed information is available in a recent EPA report (Eklund, et al., 1992).

Asphalt kilns will have similar air emission control devices as for mobile thermal desorption units, except that no VOC controls are typically employed and the air flowrates are higher requiring some differences in design parameters.

A majority of LTTD control devices use an off-gas treatment system consisting of a cyclone, an afterburner, and a baghouse (fabric filter). The cyclone is used to reduce the particulate loading on downstream devices. The baghouse may be placed before or after the afterburner; it efficiently removes particulates to low levels. The afterburner oxidizes organics and carbon monoxide by thermal destruction. Some LTTD systems use an afterburner followed by a quench chamber and a venturi wet scrubber. This system is capable of controlling acid gases if they are a concern. Some systems collect the organic contaminants, as shown in Figure 4-2, rather than destroying them.

4.5.1 Particulate Removal

Off-gases from the desorber typically pass first through a particulate control device. Particles that become entrained in the off-gas stream may be removed with cyclones, venturi scrubbers, or fabric filters. Collected particulates are usually returned to the incoming waste stream and retreated with the soil.

Cyclone collectors remove particles by creating a vortex from the inlet gas stream velocity. Centrifugal acceleration forces entrained particles outward where they collide with the wall and fall to a collection point.

Venturi scrubbers are sometimes used to treat desorber off-gas, and efficiently remove particles greater than 0.5 μm in diameter using an aqueous stream. The performance is not affected by corrosive, sticky or flammable particles, but high collection efficiencies require a higher pressure drop and thus more costly operation (Sink, 1991). The scrubber may also serve as the initial condensation stage for water and organic compounds.

The fabric filter may be a series of fine-mesh synthetic fabric similar to the type used in asphalt batch plants. An induced draft fan can be used to draw the exhaust gas through a filter. The filter may be a jet-pulse design such that high pressure (80 psig) air periodically removes accumulated particulates to collections bins. Dust from the bins may then be combined with the contaminated soil for reprocessing. The maximum allowable pressure drop across the filter may be 15 inches of water (Weston, 1990), though 3 to 8 inches of water is typical.

4.5.2 Condenser

The most important aspect of using condensers to remove VOCs from a vapor stream is designing the condenser to most efficiently remove the specific contaminants present. This physical separation process operates on the basis of the contaminants' vapor pressures which vary widely. By reducing temperature or increasing pressure until the saturation vapor pressure is reached, the vapor condenses to a liquid phase and is treated accordingly. Contaminants with high vapor pressures require correspondingly low condensation temperatures. In these situations, a quencher that removes a large portion of the moisture present often precedes the condenser to prevent icing. The coolant may be air, ambient water, brine, chilled water, or refrigerants. A separator directs the vapor/gas and liquid streams to appropriate control systems.

4.5.3 Liquid Phase Treatment

The liquid from the condenser is sometimes partially treated on-site. The liquid is separated by a gravity oil/water separator. The insoluble light organic fraction is skimmed off the top, placed into 55 gallon drum and stored for off-site treatment. The contaminated water from the separator is passed through carbon adsorption columns and then used for dust control (Weston, 1990).

4.5.4 VOC Control by Afterburner

Fume incinerators (i.e., afterburners) are often used for the control of VOC emissions from thermal desorption systems, especially for systems used for treating underground storage tank sites. An afterburner used in one system identified in the literature is a 3.5 million BTU/hr gas-fired fume incinerator, but afterburners may use up to 40 million BTU gas per hour. Typically, afterburners operate at 1400-1800°F and have a residence time of 0.5-2 seconds. The air that carries the vaporized contaminants serves as the combustion air. The flame vortex exposes the VOCs to temperatures and turbulence necessary for complete combustion. A combustion air fan maintains a minimum of three percent excess oxygen exiting the afterburner. Exhaust gases leaving the afterburner are sometimes mixed with ambient air to be cooled and then passed through a scrubber (Weston, 1990).

4.5.5 VOC Control by Carbon Adsorption

Often used as a polishing process after other treatments, carbon adsorption works on the principle that contaminants are physically adsorbed onto the activated carbon. No chemical change or reduction of the waste amount occurs. Absorption processes can occur in either the liquid or vapor phase. Regeneration or disposal of spent carbon may also produce emissions, though this is very rarely done on-site.

A liquid phase carbon adsorption usually treats water with low contaminant concentrations with a two-stage system. Clean water is often used to cool discharge solids from the desorber and suppress dust formation (Nielson et al, 1989).

4.5.6 Scrubber

Exhaust gases from thermal destruction processes may be treated in a scrubber to remove particulates or neutralize acid gases. Wet scrubbers use a liquid to absorb pollutants from a waste gas stream; the process is enhanced through a large liquid/gas contact surface area. Wet scrubbers operate by either chemical, absorption (reaction between pollutant and liquid), or physical absorption (pollutant trapped by liquid). Dry scrubbers operate by chemical absorption. Acid gases are not typically a concern when processing petroleum contaminated soils due to low concentrations of halogenated compounds (Troxler, et al. 1992). Particulate scrubbers (venturis) can be employed to capture the particles by impingement and agglomeration with liquid droplets. If a wet scrubber is used to treat the off-gases, a liquid separator is needed downstream of the scrubber, such as a cyclone or mist eliminator.

4.5.7 Miscellaneous System Adaptations and Control Approaches

Other emissions control techniques include using treated water for dust control and using ultraviolet light. Ultraviolet rays have been used to destroy dioxin in the condensate from the thermal desorption of contaminated soils.

While conducting a pilot study of the McKin Superfund site in Gray, Maine, Canonie Environmental Services Corporation made efforts to control VOC and dust emissions from excavation and aeration processes. The soil was contaminated with trichloroethylene (TCE). Excavation down to 40 feet was conducted with a kelly bar caisson rig fitted with a digging bucket and attached to a 100-foot crane. Soils discharged from the digging bucket entered a front end loader equipped with a removable plastic cover. Cylindrical steel caissons were augered into the deep excavation holes to prevent further volatilization (Webster, 1986).

4.6 Capital and Operating Costs for Remediation

Because thermal desorption is virtually never used without controls, the costs reflect emissions controls as well as remediation. Most thermal desorption units offered by vendors are predesigned systems with VOC and particulate controls already installed. This is especially true for portable systems which are typically housed on flat bed trailers. Asphalt plants do not typically have VOC controls, but if they have been modified to treat soils, the organic control device may already be added. The costs for treatment of soils contaminated with petroleum hydrocarbons typically range from $50 - 125/ton for low temperature thermal screw units and from $35 - 100/ton for rotary dryers (Troxler, et al. 1992).

IT Corporation performed a pilot study cleanup of PCBs on the Rosemount Research Center site of the University of Minnesota and in its report estimated that direct operating costs for a full-scale systems would be about $80/ton based on a 10 ton/hour system treating soil with 20 percent moisture. This figure includes $60/ton for labor, utilities, fuel, materials and supplies, and administrative costs as well as $20/ton for depreciation. These are hopper to hopper treatment costs; total costs are likely to be $175 to $350 per ton (Troxler, personal communication, 1992). Costs depend on the contaminants present and site conditions. Cost estimations should take into consideration planning and procurement, permitting, site preparation, equipment mobilization, equipment erection/startup, operations, equipment demobilization, and site closure (Fox, et al, 1991).

Soil contaminated with Herbicide Orange at the Naval Construction Battalion Center (NCBC) in Gulfport Mississippi was treated with the IT Corporation's pilot-scale thermal desorption/ultraviolet apparatus. The costs summarized below include the cost of ultraviolet destruction technology which is not typically a part of the thermal desorption process (Helsel and Thomas, 1987):

Cost of treating dioxin-contaminated soil with TD/UV Photolysis

Amount of Soil (tons)	Total Cost (millions of $)	Cost
10,000	6.002	$600/ton
20,000	8.030	$402/ton
40,000	11.796	$295/ton

Remediation Technologies, Inc. estimates the cost of treating oily soils and sludges to be in the range of $100-$300/ton of feed. The costs depend on quantity of waste, term of the contract, and moisture and organic content of the contaminated soil. Estimated costs for some other systems are presented in Table 4-5. The installed cost of complete thermal desorption systems which include treatment of off-gases and condensates is usually about two to four times the cost of the thermal units themselves (Abrishamian, 1991).

4.7 Capital and Operating Costs for Emission Controls

Costs for emission controls are included in the remediation costs given in Section 4.6. The relative contribution of emission controls to the total costs are not known. This information for selected thermal desorption systems is currently being collected under the EPA SITE program and should be publicly available in 1992.

A cost estimate was determined for some typical controls used with thermal desorption units. The cost estimate was calculated from procedures outlined in various U.S. EPA documents. These values were also compared with vendor quotes. The estimation was performed for gas flow rates of 5,000, 15,000, and 40,000 acfm. The total capital investment was determined for both mechanical shakers and pulse-jet fabric filters and includes equipment and installation costs. Site preparation and construction costs are not included in this figure. The results are presented in Table 4-6.

Table 4-5.

Remedial Costs for Various Thermal Desorption Units

System	Cost ($/ton feed)	Soil Characteristics	Soil Feed Rate
X*TRAX™, Chemical Waste Management	150-350	30% moisture; <10% organics	--
LTTA, Canonie Environmental Services, Corp.	80-150	---	30-50 tons/hr
LT^3, Roy F. Weston	100-120	20% moisture; 10,000 ppm organics	20,000 lb/hr

SOURCE: Johnson and Cosmos, 1989

Table 4-6.

Cost Information for Fabric Filters

Filter Type	Flow Rate (acfm)	Estimated Capital Cost[c] (1992 $)	Vendor Estimates[b]
Mechanical Shaker	5,000	159,000	24,000[a]
	15,000	298,000	36,400[a]
	40,000	509,000	--
Pulse-Jet Fabric Filter	5,000	124,000	30,000[a]
	15,000	205,000	52,000[a]
	40,000	456,000	--

[a] Dustex Corporation

[b] Typical cost from Soil Purification Inc. given as $250-350,000 for a pulsed-jet fabric filter for a "typical" size portable system.

[c] Estimated capital costs based on correlations given in the OAQPS Control Cost Manual (Vatavuk, 1990).

The cost estimation for an afterburner, or thermal oxidizer, was based on similar flow rates (5,000, 15,000, and 40,000 scfm). Two cases were considered for each flow rate: a) no heat exchanger (no heat recovery from the thermal oxidizer) and b) 50% heat recovery. The cost estimates and vendor information are summarized in Table 4-7. As stated earlier, thermal desorption units are typically sold as a predesigned unit that already incorporates the control devices into the total cost of the system.

4.8 Equations/Models for Estimating Emissions

Theoretical models based on fundamental principles have been proposed for predicting the evolution of volatile compounds from soil in the thermal desorption process (Lighty, et al, 1990). Both particle desorption and bed desorption were examined. The models are partial differential equations based on mass and energy balances and on the Freundlich isotherm equation. In practice, an assessment of the applicability of thermal desorption for a given site will not be based on modeling calculations, but will be based on the types of contaminants present in the soil, the physical properties of the soil, and the results of any bench-, pilot- or full-scale test runs. In most cases, the process conditions such as temperature and residence time can be modified to yield the desired removal efficiency, though heavier weight petroleum fuels such as No. 6 fuel oil may present problems for systems with relatively low operating temperatures. The cost to operate at these process conditions, however, will dictate whether or not thermal desorption is competitive with other remediation options.

Using removal efficiencies obtained from test runs, a mass balance yields the following equation to estimate an emission rate for a volatile compound leaving the desorber. This estimate does not include emissions from excavation or other handling of contaminated soil nor does it include fugitive emissions from the desorber system or from liquid and solid phase waste streams. Combustion gases from the heating system and exhaust gases from afterburners produce additional emissions not taken into account by this estimation method.

Table 4-7.

Cost Information for Thermal Oxidizers

Heat Recovery (%)	Flow Rate (scfm)	Estimated Capital Cost[c] (1992 $)	Vendor Estimates[b]
0	5,000	156,000	100,000[a]
	15,000	209,000	300,000[a]
	40,000	304,000	--
50	5,000	304,000	150,000[a]
	15,000	437,000	450,000[a]
	40,000	580,000	--

[a] Conversion Technology, Inc.

[b] Typical cost from Soil Purification, Inc. given as $75-300,000 for a thermal oxidizer for a "typical" size system.

[c] Estimated capital costs based on correlations given in the OAQPS Control Cost Manual (Vatavuk, 1990).

$$ER_i = (C_i/1000)(MR)(V_i/100)(100 - CE_{i)}/100)$$

where ER_i = emission rate for contaminant i (g/hr);
C_i = concentration of species i in contaminated soil (mg/kg);
1000 = conversion factor (mg/g);
MR = mass rate of soil treated (kg/hr);
V_i = percentage of contaminant i volatilized; and
CE_i = percent efficiency of control devices.

4.9 Case Studies of Remediation and Air Emissions

The air emissions for one case are summarized below, followed by treatment effectiveness data for a number of cases. Not all the case studies are specific to soils contaminated with petroleum products, but they are included for illustrative purposes.

4.9.1 Case Study of Air Emissions From Thermal Desorption

Canonie Environmental Services Corporation conducted a pilot study of the McKin Superfund site in Gray, Maine. Air quality was monitored during the study to estimate emissions from thermal desorption treatment of contaminated soil. The results are shown below. Treatment results were presented in Table 4-3 (Webster, 1986).

Air Emissions From Thermal Desorption Treatment at McKin Superfund Site

Location	Contaminant	Concentrations
Within 2 feet of caisson bucket and front end loader	VOC	1,000 ppm
20 feet downwind of excavation (5 minute average)	VOC	5 ppm above background
Site Perimeter	VOC	0 above 2 ppm background
Upwind of site, background, surrounding residences	VOC	1-5 ppm
Site Perimeter	TCE	0.002 - 0.01 ppm
Site Perimeter	CCl_3F	0.010 - 0.018 ppm
Site Perimeter	1,2-dichloroethylene	≤ 0.02 ppm
Site Perimeter	toluene	≤ 0.02 ppm
Site Perimeter	ethylbenzene	≤ 0.02 ppm
Site Perimeter	xylene	≤ 0.02 ppm
Site Perimeter	total suspended particulates	$\geq 110 \mu g/m^3$ without controls
Site Perimeter	total suspended particulates	$\geq 50 \mu g/m^3$ with controls

4.9.2 Case Studies of the Efficiency of Thermal Desorption

Thermal desorption has been found to have high removal efficiencies for volatile and semi-volatile compounds. Described below are several cases studies with tables showing removal efficiencies as well as feed and product concentrations.

Use of X*TRAX™ on VOCs and PCBs

A laboratory-scale study of Chemical Waste Management's (CWM) X*TRAX thermal desorber treated one to two kilograms per hour of various contaminated soils. The X*TRAX system consists of a rotary kiln, scrubber, condenser, particulate filter, and carbon adsorber. The soil concentrations and removal efficiencies are presented for several contaminants (Ayen and Swanstrom, 1991).

CWM X*TRAX™ Laboratory-Scale Treatment of Contaminated Soils

Soil Type	Compound	Concentrations (ppm)		Percent Removal
		Feed	Product	
Petroleum contaminated soil	Acetone	2600	16	99.38
	Xylenes	2400	9.5	99.6
	ethylbenzene	1600	5.2	99.68
	Styrene	200	<.005	>99.99
	Tetrachloroethylene	150	0.094	99.94
	Chlorobenzene	110	0.18	99.84
	1,2-Dichloroethane	38	0.062	99.84
	Anthracene	4650	12	99.74
	bix(2-ethylhexyl)phthalate	2380	<.33	>99.99
	pentachlorophenol	497	2.8	99.44
Contaminated silt, clay, gravel	PCBs	805	17.2	97.9
	Xylenes	18.8	<.125	>99.3
	1,2,4-Trichlorobenzene	24.8	<.33	>98.7
	di-N-butylphthalate	13.2	<.33	>97.5
	pentachlorobenzene	11.6	<.33	>97.1
Non-PCB soil, sludges, and mixture clay soil	3,3-dichlorobenzidine	1716	<.66	
	nitrobenzene	42.9	<.33	
	azobenzene	3000	4.9	
	2-chloroanaline	779	ND	
	benzidine	792	ND	
Soil/sludge	3,3-dichlorobenzidine	700	<.66	
	azobenzene	44.6	ND	
	benzidine	13	ND	
Sludge	3,3-dichlorobenzidine	503	<.66	
	azobenzene	16.8	ND	

The pilot-scale unit, which treats 4.5 metric tons per day at 30 percent moisture, was used to treat various soils contaminated with PCBs. The following data were reported for three types of soil (de Percin, 1991a; Ayen and Swanstrom, 1991).

CWM X*TRAX™ Pilot-Scale Treatment of Sandy Soil with PCB's

Compound	Feed (ppm)	Product (ppm)	% Removal
PCB's	1480	8.7	99.4
1,2,4-Trichlorobenzene	2.9	not detected	>99.9
Di-n-Butylphthalate	1.0	0.24	76.0
Bis(2-Ethylhexyl)phthalate	9.1	0.18	98.0

CWM X*TRAX™ Pilot-Scale Treatment of Clay, Silt, and Gravel with PCB's

Compound	Feed (ppm)	Product (ppm)	% Removal
PCB's (Arochlor 1254)	1400	34	97.6
1,2,4-Trichlorobenzene	2800	19	99.3
Di-n-Butylphthalate	6.9	not detected	>98.0
Bis (2-Ethylhexyl) phthalate	4.7	not detected	>97.2

CWM X*TRAX™ Pilot-Scale Treatment of Contaminated Soil

Compound	Feed (ppb)	Product (ppb)	% Removal
Methyl ethyl ketone	100,900	<100	>99.9
Tetrachloroethylene	91,000	15.6	99.98
Clorobenzene	61,800	6.5	99.98
Xylene	56,400	2.8	99.99
1,4-Dichlorobenzene	78,400	1.4	99.99
1,2-Dichlorobenzene	537,000	74.1	99.99
Hexachlorobenzene	79,200	300	99.62

Study of Soil from Two Superfund Sites

In Phase II of an Environmental Protection Agency study on thermal desorption, soils from two Superfund sites were processed. A Lindberg furnace (Model 51848) was equipped with an electronic temperature controller and 1600 watt heater. Berlin-Farro and Old Mill Sites soils were processed at 350°F and 550°F with 30 minute residence times. A summary of results is shown below (Lauch, et al, 1990).

EPA Study of Berlin-Farro Site Soil

Contaminant	Feed (μg/kg)	Product (μg/kg)	% Removal at 350°F
2-Butanone (detected in blank)	290	343	<18>
Trichloroethene	147	<23	>84
Tetrachloroethene	280	<23	>92
Toluene	483	19	96
Xylenes (total)	387	<23	>94
Hexachlorobutadiene	1900	430	77
Hexachlorocyclopentadiene	46000	3050	93
Pentachlorobenzene	10200	15100	<48>
Hexachlorobenzene	105000	250000	<138>
Contaminant	**Feed (μg/kg)**	**Product (μg/kg)**	**% Removal at 550°F**
2-Butanone (detected in blank)	290	80	72
Trichloroethene	147	<25	>83
Tetrachloroethene	280	3	99
Toluene	483	27	94
Xylenes (total)	387	<25	>91
Hexachlorobutadiene	1900	<3300	--
Hexachlorocyclopentadiene	46000	<3300	93
Pentachlorobenzene	10200	2500	75
Hexachlorobenzene	105000	47000	55

EPA Study of Old Mill Site Soil

Contaminant	Feed (μg/kg)	Product (μg/kg)	% Removal at 350°F
Trichloroethene	2400	173	93
Tetrachloroethene	362	35	90
Toluene	152	43	72
Xylenes (total)	950	285	70
Aroclor 1260	2000	3000	<50>

Contaminant	Feed (μg/kg)	Product (μg/kg)	% Removal at 350°F
Trichloroethene	2400	<25	>99
Tetrachloroethene	362	<25	>93
Toluene	152	57	63
Xylenes (total)	950	48	95
Aroclor 1260	2000	not detected	>95

Use of LT^3 on JP-4 Fuel and Other VOCs at Tinker Air Forces Base

Weston's LT^3 thermal desorption system was employed in a pilot study to clean up contaminated soils at Tinker Air Force Base in Oklahoma. The contaminants were primarily JP-4 jet propulsion fuel and chlorinated organic compounds. After modifications, the residence time was set at 40 minutes and the heat transfer oil at 600°F. The system was designed to process 15,000 lbs/hour but in practice handled 30 percent more than the design specification. The emissions control system included a fabric filter, condenser, afterburner, and scrubber (Weston, 1990).

Pilot Study of Tinker Air Force Base Site

Contaminant	Feed (μg/kg)	Product (μg/L)	% Removal
Vinyl chloride	<3500	0.2	---
Dichloromethane	< 1800	0.1	---
1,1-Dichlroethene	< 1800	0.1	---
Chloroform	140[a]	0.1	>98.57
1,2-Dichloroethane	< 1800	0.1	---
1,1,1-Trichloroethane	< 1800	0.1	---
Trichloroethene	37250	0.3	99.986
Tetrachloroethene	2760[a]	0.1	>99.93

Contaminant	Feed (μg/kg)	Product (μg/L)	% Removal
2-Butanone	<11000	0.6	---
Benzene[b]	<1800	0.1	---
Toluene[b]	<1800	0.1	---
Chlorobenzene[b]	<1800	0.1	---
Ethylbenzene[b]	<1800	0.1	---
1,2-Dichlorobenzene	35000	6[a]	>98.46
1,3-Dichlorobenzene	---[c]	---[c]	>8.57
1,4-Dichlorobenzene	8700	6[a]	>63.22
Fluoranthene[b]	<3300	<10	>48.48
Benzo(a)anthracene[b]	<3300	<10	---
Benzo(a)pyrene[b]	<3300	<10	---
Benzo(b)fluoranthene	<3300	<10	---
Chrysene[b]	<3300	<10	---
Dibenzo(a,h)anthracene[b]	<3300	<10	---
Acenaphthene[b]	<3300	<10	---
Acenaphtylene[b]	<3300	<10	---
Anthracene[b]	60[a]	<10	---
Benzo(g,h,i)perylene[b]	<3300	<10	---
Fluorene[b]	<3300	<10	---
Indeno(1,2,3-c,d)pyrene[b]	<3300	<10	---
Phenanthrene[b]	<3300	<50	>41.77
Pyrene[b]	790[a]	<10	---
Benzo(k)fluoranthene[b]	280[a]	<10	---
Trichlorofluoromethane	<3300	<10	>99.43
trans-1,2-Dichloroethene	---[c]	---[c]	>99.74
m-Xylene	---[c]	---[c]	>99.89
o,p-Xylene	---[c]	---[c]	>99.82
Naphthalene	---[c]	---[c]	>96.98

[a] Not detected at the specified detection limit.
[b] Potential constituent of JP-4 fuel.
[c] Only % removal data given in report.

Use of ReTec's Thermal Screw on Semi-Volatile Organics

The ReTec pilot unit was used to remediate refinery filter cake, creosote contaminated clay, and coal tar contaminated soil, which was presented earlier. The process uses molten salt to heat the soil to 450 to 500°F, volatilizing the contaminants. Cyclones, a semi-volatile organic separator, a chilled condenser, and activated carbon beds are used to control the particulate and contaminant emissions. The following table presents the results (U.S. EPA, 1991).

ReTec's Pilot Unit

Waste Type	Compound	Concentration (ppm)		Percent Removal
		Feed	Product	
Refinery vacuum filter cake	naphthalene	<.1	<.1	
	acenaphthylene	<.1	<.1	
	acenaphthene	<.1	<.1	
	fluorene	10.49	<.1	>98.9
	phenanthrene	46.5	<.1	>99.3
	anthracene	9.8	<.1	>96.6
	fluoranthene	73.94	<.1	>99.8
	pyrene	158.37	<.1	>99.9
	benzo(b)anthracene	56.33	1.43	97.5
	chrysene	64.71	<.1	>99.9
	benzo(b)fluoranthene	105.06	2.17	97.9
	benzo(k)fluoranthene	225.37	3.64	98.4
	benzo(a)pyrene	174.58	1.89	98.9
	dibenz(a,b)anthracene	477.44	10.25	97.8
	benzo(ghi)perylene	163.53	5.09	96.6
	indeno(123-cd)pyrene	122.27	4.16	96.6
Creosote contaminated clay	naphthalene	1321	<.1	>99.9
	acenaphthylene	<.1	<.1	
	acenaphthene	293	<.1	>99.96
	fluorene	297	1.6	>99.96
	phenanthrene	409	<.1	99.6
	anthracene	113	1.5	>99.7
	fluoranthene	553	2	99.7
	pyrene	495	<.1	99.6
	benzo(b)anthracene	59	<.1	>99.99
	chrysene	46	2.5	>99.8
	benzo(b)fluoranthene	14	<.1	82.3
	benzo(k)fluoranthene	14	<.1	>99.87
	benzo(a)pyrene	15	<.1	>99.9
	dibenz(a,b)anthracene	<.1	<.1	
	benzo(ghi)perylene	7	<.1	>99.4
	indeno(123-cd)pyrene	3		>99.3

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5.0 SOIL VAPOR EXTRACTION

5.1 Process Description

Soil vapor extraction (SVE) is one method used for the treatment of soil contaminated with volatile hydrocarbons. The process is sometimes also referred to as soil venting, vacuum extraction, aeration, or in-situ volatilization. In general terms, soil vapor extraction removes volatile organic constituents from contaminated soil by creating sufficient subsurface air flow to strip contaminants from the vadose (unsaturated) zone by volatilization. Complete removal may not be possible unless the source of vapors (e.g. hydrocarbon lens on groundwater) is also removed. As the contaminant vapors are removed, they may be vented directly to the atmosphere or controlled in a number of ways. Soil vapor extraction has been widely used to remediate sites contaminated with gasoline or chlorinated solvents (e.g. TCE). It is also sometimes used to minimize migration of vapors into structures or residential areas during other types of remediation. By its nature, SVE is an on-site, in-situ treatment method. It is often used in conjunction with or following other remedial measures such as excavation of subsurface waste bodies, removal (pumping) of any hydrocarbon lens that is present, or air stripping of contaminated ground water.

A number of reports and articles have recently been published that provide useful information regarding SVE systems. The best single source of information is a recent EPA report (Pedersen and Curtis, 1991). Much of the information in this section was drawn from that report and a second EPA report (Thompson, et al, 1991). Other key references are three studies that include summarized information about existing SVE systems in use at field sites (Crow, et al, 1987; Hutzler, et al 1989; and PES, 1989), an evaluation conducted under EPA's SITE program (Michaels, 1989), and a recent overview paper (Johnson, et al., 1990). The Johnson, et al. paper is given as Appendix E of this report.

The relative advantages of SVE over other remediation approaches are:

1) The equipment is readily available and simple to install and operate;
2) Large volumes of soil can be treated in a cost-effective manner;
3) Remediation can proceed in many cases without disrupting on-going commercial activities at the site; and
4) Air emissions are released from a point source and thus can readily be controlled.

The major disadvantages of SVE versus other remediation approaches are that:

1) The method is not applicable for saturated soils or soils with low air-permeabilities;
2) The success of the method varies with the volatility (vapor pressure) of the contaminants present; and
3) Significant residual contamination may remain in the soil after treatment under some remediation scenarios.

The success of SVE for a given application depends on numerous factors with the three key criteria being: 1) the nature of the contamination; 2) the behavior of subsurface vapor flow at the site; and 3) regulatory requirements. Each of these criteria is described below. A simplified decision guide for judging the applicability of SVE is shown in Figure 5-1.

Spills or leaks of fuels typically involve liquids containing dozens of different constituents. For removal by SVE to be effective, the contaminants generally must have vapor pressures greater than 1.0 mm Hg at 20°F. The tendency of the organic contaminants to partition into water or to be adsorbed onto soil particles also affects SVE effectiveness, so the compound's water solubility, Henry's Law constant, and soil sorption coefficient are of interest. The soil temperature affects each of these variables and hence the rate of vapor diffusion and transport. The concentration of contaminants that are initially present will also affect their relative partitioning between vapor and liquid phases, and the amount that is solubilized or adsorbed. The time that the

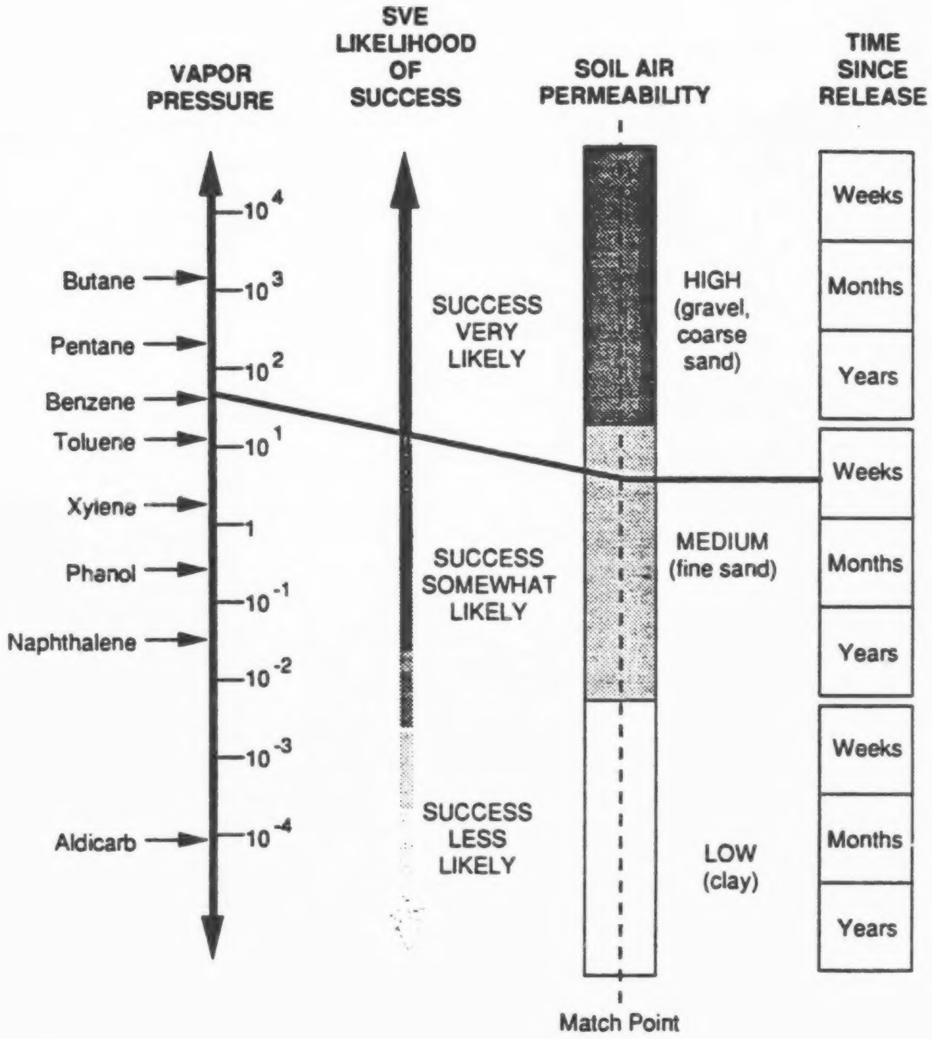
VAPOR PRESSURE
SVE LIKELIHOOD OF SUCCESS
SOIL AIR PERMEABILITY
TIME SINCE RELEASE
10^4
Butane
10^3
Pentane
10^2
Benzene
Toluene
10^1
Xylene
1
Phanol
10^-1
Naphthalene
10^-2
10^-3
Aldicarb
10^-4
SUCCESS VERY LIKELY
SUCCESS SOMEWHAT LIKELY
SUCCESS LESS LIKELY
HIGH (gravel, coarse sand)
MEDIUM (fine sand)
LOW (clay)
Weeks
Months
Years
Weeks
Months
Years
Weeks
Months
Years
Match Point

Figure 5-1. Simplified Guide to Applicability of Soil Vapor Extraction.

Source: (Pedersen and Curtis, 1991)

contamination has been present is also an important factor, as mixtures of contaminants will generally become depleted of their more volatile components over time through volatilization. This process, referred to as weathering, will tend to cause SVE to become progressively less applicable as the site ages. It also affects the operation of the SVE system, as the more volatile components are typically removed first and the composition of the vapors collected and treated varies over time.

Although SVE may be used in a variety of soil types, the effectiveness will depend on the ability of air to flow through the soil. The ability of vapors to flow through a porous media such as soil is usually defined as the air permeability. Any factors that influence the air permeability of the soil, such as soil porosity, grain size, moisture content, depth to ground water, and stratification must be taken into consideration when planning this type of remediation. The presence of cracks, inadequately grouted boreholes, or other subsurface conduits will alter the subsurface flow patterns. Soil vapor extraction may not be practical for sites where the source of vapors is deep underground (e.g. >100 feet), in areas with shallow groundwater tables (e.g. <10 feet) or at sites where the groundwater level fluccuates greatly over time.

The types of contaminants present and the clean-up criteria will affect the cost-effectiveness of SVE versus other remediation options. The final cleanup level for contaminants in the soil will dictate whether or not SVE is a viable option. Very stringent cleanup levels may dictate excavation of the soil and further on-site treatment. Air emission regulations may require the use of controls to reduce the level of contaminants in the exhaust gas. The cost of such emission controls may influence the overall selection of a remediation approach.

A few potential problems may arise in implementation of soil vapor extraction, but effective solutions to most problems exist. When there is some concern that contaminant vapors from a nearby site may be drawn in by the vacuum, air inlet wells may be placed around the perimeter of the site to limit remediation to the site under treatment. To avoid channelized flow, butterfly or ball valves may be placed on the extraction wells so that they may be shut down if necessary. If contaminated water is extracted in the process, a liquid phase treatment system is usually installed.

Evidence of unusually high carbon dioxide levels indicates that some sites may experience enhanced subsurface biodegradation that may be partially or wholly a result of soil vapor extraction. Subsurface air flow may promote growth of aerobic hydrocarbon degraders which feed on the organic contaminants by improving the level of available oxygen for the microbes. At one site, carbon dioxide concentrations in the soil gas were 8.5%; much higher than the 0.03% or 0.04% typically present in the atmosphere. Rough calculations indicated that up to 40% of the gasoline was destroyed by degradation. Other sources of organic material such as co-disposed municipal waste were not considered and may have been partially responsible for the high carbon dioxide levels.

Figure 5-2 shows a generalized process flow diagram for the soil vapor extraction process. Typical systems include extraction wells, monitoring wells, air inlet wells, vacuum pumps, vapor treatment devices, vapor/liquid separators and liquid phase treatment devices. Wells are generally 4 to 8 inches in diameter. An option sometimes employed is to introduce the air at the air inlet well into the saturated zone (i.e. groundwater table). This technique, referred to as air sparging, acts to strip some of the volatile and semi-volatile compounds from the ground water. Another option is to heat the air entering the inlet wells to enhance the volatilization of less volatile, higher molecular-weight contaminants, such as diesel fuel.

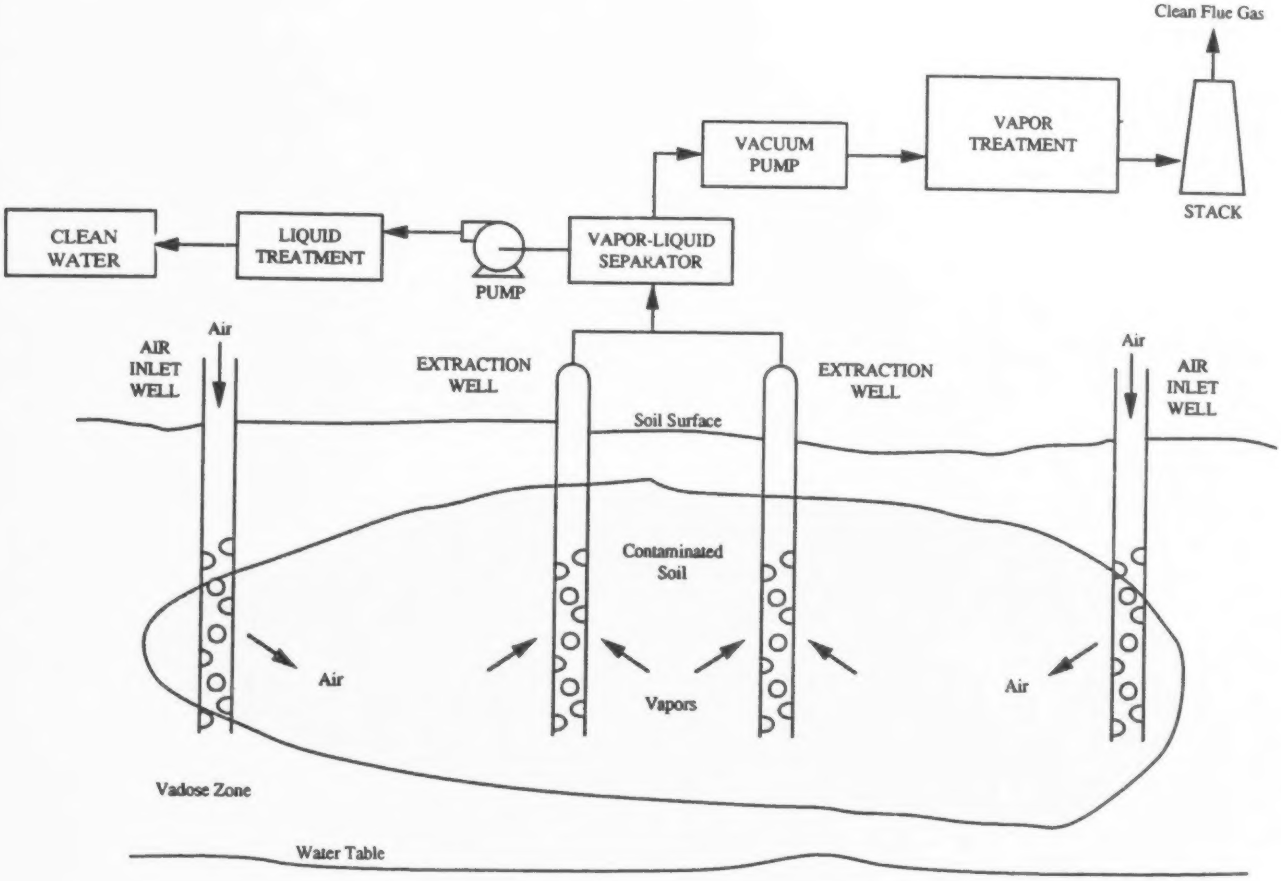
Clean Flue Gas
VAPOR TREATMENT
VACUUM PUMP
STACK
CLEAN WATER
LIQUID TREATMENT
PUMP
VAPOR-LIQUID SEPARATOR
AIR INLET WELL
Air
EXTRACTION WELL
EXTRACTION WELL
Air
AIR INLET WELL
Soil Surface
Contaminated Soil
Air
Vapors
Air
Vadose Zone
Water Table

Figure 5-2. Generalized Process Flow Diagram for Soil Vapor Extraction.

5.2 Identification of Air Emission Points

The air emissions associated with soil vapor extraction systems come primarily from the stack. Stack heights are typically 12-30 feet and usually only one stack is used. Additional releases of volatile organics may occur from the treatment of any contaminated water that is extracted. Fugitive emissions are considered negligible due to the negative pressure throughout most of the system.

5.3 Typical Air Emission Species of Concern

Emissions include untreated volatile organics from the extraction process. Removal and emissions of semi-volatile organic compounds will also occur, though with less efficiency than for VOCs. Lesser amounts of air emissions associated with the control system may also occur. Due to the variety of technologies used, stack emissions may include products of incomplete combustion, nitrogen oxides, particulate matter, carbon monoxide, acid gases and any other possible products of these technologies. Of primary concern, however, are the volatile organics emitted from the point sources.

5.4 Summary Of Air Emissions Data

Air emissions data for several SVE systems are summarized in Table 5-1. The data are from a variety of soil vapor extraction systems. Overall there is little detailed published information about SVE systems, making it difficult to assess the representativeness of this sample.

The emission rate of VOC compounds over time from continuously operated SVE systems tends to show an exponential-type decay curve. If the system is stopped and then restarted, however, the VOC emission rate returns to near the original rate unless the remediation is nearing completion. Apparently, shutting off the vacuum allows the soil-gas equilibrium to become re-established. Due to this behavior, the most

Table 5-1.

Summary of Emissions Data for SVE System

Source	No. of Systems Surveyed	Parameter	Units	Range or Value	Approximate Average
Crow, et.al. (1987)	13	Flowrate per well	cfm	5.3 - 300	80
		Removal	lb/day	2 - 250	60
		Exhaust Gas Concentration	ppmv	20 - 350	100
Hutzler, et.al. (1989)	19	Total Flowrate	cfm	3 - 5,700	800
		Treatment: - None - Carbon - Catalytic Incineration - Combustion	# systems	 9 6 1 1	
		Removal Rate	lb/day	4 - 430	100
PES (1989)	17	Total Flowrate	cfm	25 - 11,300	2,200
		Pollutant Concentration	ppmv	150 - 38,000	4,000
		Control Efficiency	%	90 - 99	95

efficient method of operation is to run the SVE system only for a part of each day or week, i.e. operate in a "pulsed" mode.

Published emission factors for SVE systems based on typical operating conditions are (Thompson, et al, 1991):

Uncontrolled Emissions:	25,000 g/hr 250 kg/day (based on 10 hours of operation)
Controlled Emissions:	1,250 g/hr 0.05 g/g VOC in soil

5.5 Identification of Applicable Control Technologies

As the vapors are removed from the soil they are either discharged to the atmosphere or treated to reduce air emissions. If the hydrocarbon content is high enough, direct combustion is theoretically possible. However, because concentrations typically drop significantly during removal, natural gas or some other fuel will be needed to maintain combustion. Also, for safety reasons, dilution air is typically added to maintain the VOC concentration below the lower explosive limit (LEL). In some cases, the wells may be shut down for a period of time to allow subsurface vapor pressures to re-equilibrate, thus yielding concentrations sufficient to sustain a flame. For lower levels of hydrocarbons, catalytic oxidation may be effective. Carbon adsorption systems are often used but they may be costly to implement and are generally not acceptable for high-humidity gas streams.

A recent survey indicates that the exhaust from about 50% of SVE systems is vented directly to the atmosphere with no controls (PES, 1989). The trend, however, is for VOC controls to be required. For those systems with controls, the most viable options are:

1) activated carbon adsorption;
2) catalytic oxidation;
3) thermal incineration;
4) internal combustion engine; and
5) miscellaneous control approaches.

The first three treatment options are the most commonly used for large SVE systems such as those used at Superfund sites or refineries. Internal combustion engines (ICE) are a common choice for control of emissions for small systems such as those used at Leaking Underground Storage Tank (LUST) sites. Removal efficiencies of 95-99% for VOCs should be theoretically achievable with any of these control options.

No single control method is preferred. Each has advantages and disadvantages that must be considered for each specific application. Control options are discussed below. Further information is available from EPA's Center for Environmental Research Information (CERI) (Eklund, et al., 1992).

5.5.1 Carbon Adsorption

Carbon adsorption using activated granular carbon (GAC) is the most common control method for SVE systems. VOCs are removed by being physically trapped on the surface of the GAC or by chemical reactions with the carbon. The efficiency of GAC is due to its very large surface area per unit mass. Two options for GAC systems are available: 1) "throw away" systems, and 2) fixed bed regenerable systems. In the first option, canisters of GAC are used and disposed of or reactivated off-site. In regenerable systems, steam or hot air is used to strip contaminants from the GAC in place. The contaminants are recovered as a liquid. The cost-effectiveness of regenerable systems will increase as the treatment time and the mass of contaminants to be treated increase.

Modular, skid-mounted treatment systems are available from numerous vendors. Prefabricated GAC units containing up to a ton of carbon are available. Flowrates over 1,000 scfm can be accommodated.

The primary advantage of carbon adsorption over other control options is that the control efficiency of GAC systems is not significantly affected by the changes in air flowrate and VOC concentration that typically occur at SVE sites. It is applicable to most contaminants having molecular weights between 50 and 150; lighter compounds tend to pass through the GAC unabsorbed and heavier compounds tend to bind permanently to the carbon and cannot be desorbed. GAC tends to be the control method of choice for SVE systems with low VOC concentrations in the exhaust gas (e.g. less than 500-1000 ppmv).

Carbon adsorption has several limitations that may be significant for SVE applications. One, water vapor will occupy adsorption sites and reduce the removal capacity. It is usually recommended that the gas to be treated have a relative humidity of less than 50% for GAC to be effective. Two, carbon tends to not retain organics at temperatures exceeding 150°F. This temperature is well below the temperatures of 200 to 800°F in the exhaust gas that can be caused by compression of air caused by the removal pump. The air can be cooled or pumps used that don't add much heat to the system (e.g., liquid ring seal pumps). Three, high mass loadings of VOCs in the exhaust gas will cause the carbon to quickly be exhausted and result in high costs to replace or regenerate the carbon. The first two limitations can be off-set through modifications to the system design, but these modifications will increase the cost of remediation.

5.5.2 Thermal Incineration

Thermal incineration can be used to destroy vapor-phase contaminants. Contaminant-laden vapors are heated to temperatures above 1000°F via a direct flame or a combustion chamber. The method is applicable to a wide range of compounds and over a large range of concentrations. It is not, however, widely used for SVE applications except for large-scale, long-term clean-ups. For the flame to be self-sustaining, the VOC concentration needs to be at percent levels that may be above the lower explosive limit for the contaminant of concern. For lower VOC levels, auxiliary fuel such as methane or propane must be added. The cost of this fuel can be prohibitive. The efficiency of the method is also affected by changes in the flowrate. As the flowrate varies from design conditions, the mixing and residence times in the incinerator will vary and decrease the destruction efficiency.

5.5.3 Catalytic Oxidation

Catalytic oxidation, also called catalytic incineration, is similar in design and operation to thermal incineration except that a catalyst is present that enhances combustion. The catalyst is usually palladium or platinum in a metallic mesh, ceramic honeycomb, or catalyst-impregnated beads in a packed bed. The catalyst allows destruction to occur at lower temperatures than for thermal incineration (600-900°F). There is therefore less auxiliary fuel required and commensurate lower fuel costs.

Design efficiencies of 95 to 99 percent are typical. The catalyst can be damaged by overheating, so the air stream must be diluted, if necessary, to a VOC concentration below about 3000 ppmv, to maintain acceptable operating temperatures. Maintenance of this VOC level raises the capital and operating cost of the system since accurate monitoring of the gas stream is needed as is the ability to control the dilution of the gas stream. As for thermal incinerators, catalytic oxidation systems function best when the flowrate is constant.

The catalyst will become less effective over time and can be adversely impacted by trace contaminants in the gas stream. Depending on the type of catalyst employed, it can be damaged by chlorinated hydrocarbons, mercury, phosphorus, or heavy metals.

5.5.4 Internal Combustion Engines (IC)

Industrial or automotive engines have been widely used to control VOC emissions from SVE systems. Depending on the engine size, air flows of 30 to 100 scfm have been treated. The effective flowrate is reduced, however, if ambient air must be added to the air stream to add sufficient oxygen to support combustion. As with other thermal treatment methods, supplemental fuel is needed.

Destruction efficiencies of 99+% have been reported for the most common components of gasoline (Pedersen and Curtis, 1991). Advantages of IC engines as controls are that the systems are portable, they can handle very concentrated air streams without the need for dilution, and the engine can provide power to operate the SVE system. Disadvantages are that the systems can only treat small flowrates and that manual supervision is required for a period during start-up to set the flowrates and operating conditions. Emissions of nitrogen oxides from the engine may be a concern in some locales.

5.5.5 Miscellaneous Control Approaches

A number of additional control devices may potentially be applicable for controlling VOC emissions from SVE systems, including condensers, packed bed thermal processors, and biofilters. Condensers using chilled water or other refrigerants can remove anywhere from 50 to 90% of VOCs from concentrated streams (>5000 ppmv VOCs). Packed bed thermal processors consist of a bed of ceramic beads heated to 1800°F that is used to destroy organics and chlorinated hydrocarbons. Biofilters consist of soil beds that trap VOCs in a manner analogous to GAC and then are regenerated by biological action. Biotreatment requires time to establish an active culture of microbes and careful control of soil moisture, temperature, and air flow patterns to maintain the efficiency of the microbial action.

5.6 Costs For Remediation

The costs to install and operate an SVE system will, of course, vary from site to site. A typical cost to install and start-up a small system is less than $100,000 (Newton 1990). Total capital costs for equipment range from $65,000 to $135,000 excluding the cost of each vapor-recovery well (Cochran, 1987). Typical capital costs for the major components of the system (Pedersen and Curtis, 1991) are $2,000-4,000 per well, $10,000 or more for a large (25hp) blower/fan, $2,500 for an air/water separator, and $10,000 for a structure to house the system. A major variable is the cost of any monitoring and control system needed to maintain the VOC level in the exhaust stream within preset limits.

Typical operation and maintenance costs are $6,000 to $26,000 per year (Cochran, 1987). The major operating costs (Pedersen and Curtis, 1991) are for power, VOC controls, monitoring, and labor. Power costs for a 10hp system are estimated to be about $20 per day. VOC control costs are discussed in the next subsection. Monitoring and labor costs are highly variable. In general, operating costs in these areas can be minimized through the use of automated monitoring and control equipment. The optimal split for this trade-off between capital and operating costs will depend on the duration of the remediation and the proximity of the site to the labor source.

5.7 Costs For Emission Controls

Equations for predicting the costs of emission controls based on system design parameters are available (PES, 1989). Typical costs for various types and sizes of treatment systems are given in Table 5-2. The cost estimates are drawn from a number of vendors and therefore a range is shown in most cases. The costs from different vendors may not be directly comparable since the cost basis may vary. For example, regenerable carbon adsorption systems cost from $22,000 to $55,000 for manually regenerated systems and $165,000 for a fully-automated equivalent system. The cost data are intended to show the general level of costs likely to be incurred for various types of control options.

Table 5-2.

Summary of Capital Costs to Control VOC Emissions From SVE Systems

Treatment	Maximum Flow (scfm)	Capital Cost ($)
Carbon Adsorption (Regenerable)	105	20,000
	250	24,000
	500-600	9,000 - 33,000
	1100	12,000
Thermal Incineration	100	25,000
	570	44,000
Carbon Canisters	100	700
	500	8,000
	1000	6,000
	4000	23,000
Catalytic Oxidation	100	25,000
	200	31,000 - 69,000
	500	44,000 - 86,000
	1000	77,000 - 94,000
	5000	220,000
		+ 20,000 for dilution system
Internal Combustion Engine	45	62,000
	100	50,000

Source: Adapted from Pederson and Curtis, 1991.

Maintenance costs will vary depending on the type of system and may include power, fuel, activated carbon, and the associated labor. The costs will vary with the size of the system and the operating rates. Electricity to run the blower motor are about $600 per month for a 10 hp blower. Fuel costs for thermal incineration and catalytic oxidation depend on the VOC concentration of the influent air. Typical costs are $500 to $1,000 per month. Auxillary fuel costs for IC engines are also about $500 to $1,000 per month. Activated carbon will cost from $1 to $2 per pound. Typical carbon costs are about $25 per pound of hydrocarbons removed (about $160 per gallon).

5.8 Equations and Models For Estimating VOC Emissions

The factors that govern vapor transport in the subsurface are very complex and no practical, accurate theoretical models for predicting emissions or recovery rates for SVE systems exist. During operation of SVE systems, the vacuum that is applied to the soil and the resulting pressure gradient is the dominant factor in determining the flow rate of vapors. The induced vacuum in the soil decreases with distance from the extraction well and a radius of influence exists that defines the extent to which vapors can be drawn to the well. The length of this radius depends on the strength of the vacuum source; soil properties such as porosity, permeability, and moisture content; and site properties such as surface coverings. In practice, field tests are typically performed to evaluate the potential effectiveness of SVE for a given site. The field tests may be either a pilot-scale demonstrations of SVE or tests of the air permeability. This information is used to determine the number of wells required to remediate the site and the spacing of the wells.

Subsurface vapor flow equations based on Darcy's Law have been published that predict the flow rate of vented gas (Johnson, et al, 1990). The key inputs are the air permeability of the soil, the air-filled porosity of the soil, the thickness of the soil layer, the density of the vapor, and the gradients of pressure and vapor concentration. Methods for measuring the air permeability are based on measuring the difference between the ambient atmospheric pressure and the air pressure in the soil during vapor transport. Johnson, et al (see Appendix E) describe a test where air is withdrawn from a well at a constant flow rate while the draw-down (vacuum) pressure is measured in a monitoring well some distance away. The pressure is plotted versus the log of time and the slope of this equation is the air permeability. Measurements at several monitoring well locations are needed. Similar test methods may also be employed such as air injection tests and oil field tests such as pressure buildup and draw-down tests (Pedersen and Curtis, 1991).

Using data from pilot-scale tests at the site, air emissions can be estimated with the following mass balance equation (Eklund, et al, 1992):

(Eq. 5-1)

$$ER = (C_g)\left(\frac{Q}{60}\right)(10^{-6})$$

where:
ER = Emission rate (g/sec);
C_g = Concentration in extracted vapors ($\mu g/m^3$);
Q = Vapor extraction rate (m^3/min);
$1/60$ = Conversion factor (min/sec); and
10^{-6} = Conversion factor ($g/\mu g$).

The extraction rate, Q, can be estimated from the results of pilot-scale tests at the site if any changes in pump size and number of wells between the pilot- and full-scale systems are taken into account. If no pilot-scale data are available, results of field test of soil-air permeability can be used to estimate Q. If these too are not available, a default value can be used for the extraction rate. Typical flow rates for Q at Superfund sites range from 14 m^3/min (500 cfm) to 425 m^3/min (15,000 cfm), with a typical default value being Q = 85 m^3/min (3,000 cfm).

The contaminant concentration in the extracted vapors, C_g, can also be estimated from the results of pilot-scale tests at the site. The second best approach is to estimate C_g by collecting samples of the headspace vapors above the contaminated soil and measuring the concentration of the compound(s) of interest. These equilibrium soil-gas samples can be collected using ground (soil-gas) probes or by transferring soil samples from split-spoon samplers (to minimize VOC losses) to sealed containers and allowing the headspace to equilibrate.

Field data are required to get an accurate value for C_g. If no field data are available, however, a very conservative value for C_g can be estimated by assuming that the soil-gas is saturated. The maximum vapor concentration of any compound in the extracted vapors is its equilibrium or "saturated" vapor concentration, which is calculated from the compound's molecular weight, vapor pressure at the soil temperature, and the ideal gas law:

$$C_g = \frac{(Pvap)(MW * 10^9)}{((R)(T))} \qquad \text{(Eq. 5-2)}$$

where:
C_g = Estimate of contaminant vapor concentration ($\mu g/m^3$);
Pvap = Pure component vapor pressure at the soil temperature (mm Hg);
MW = Molecular weight of component i (g/mole);
R = Gas constant = 62.4 L-mm Hg/mole -°K;
T = Absolute temperature of soil (°K); and
10^9 = Conversion factor ($\mu g\text{-}L/g\text{-}m^3$).

Values of molecular weight, vapor pressure at 25°C, and saturated vapor concentration at 25°C are given in Appendix A. It is important to note that Equation 5-2 gives the theoretical maximum value of C_g. It will overpredict C_g for any compounds present in the soil at relatively low concentrations. Equation 5-2 will also overpredict the long-term average value of C_g since the concentration of contaminants in the gas extracted using a SVE system will tend to drop over time. It can drop by more than 95% in the first two days of operation, though pulsed operation will allow the soil-gas concentration to be periodically re-established at levels near the initial concentration.

Equation 5-2 assumes that an infinite source of vapors exists and that the contaminants are present in the soil or ground water at relatively high concentrations (e.g., total hydrocarbons of 500 ppm in the soil). Therefore, the vapor-phase concentration for a given compound is independent of the concentration of that same compound in the soil/liquid matrix.

Removal rates can be 500-600 kg/day or higher and control efficiencies (when applicable) range from 60-99%. As previously mentioned, only about half of the sites listed used any VOC control equipment.

5.9 Case Study

Process Description

Terra Vac Incorporated has developed a vacuum extraction system designed to remove volatile organic contaminants from the vadose zone. At the Groveland, Massachusetts Superfund site, the contaminated air stream was treated with two sets of activated carbon canisters (Michaels, 1989 and Stinson, 1989). Due to weather conditions, liquid water was extracted as well, so a vapor-liquid separator was included to remove contaminated water to a holding tank. The process design is shown in Figure 5-3. No air inlet wells were used at this site.

Characterization of Air Emissions

Because no biodegradation was taking place in this case, the compounds released to the atmosphere were the same as those found in the soil. By far the most predominant contaminant removed was trichloroethylene, although 1,1,1-trichloroethane, trans-1,2-dichloroethylene, and tetrachloroethylene were also extracted.

Emission Factors

Table 5-3 shows emissions factors for each of the four contaminants. The estimated total VOC peak emission factor is 9.57 g/hr. Based on the field data, the carbon adsorption control device had an efficiency of better than 99%. Because the contaminated water was not treated on-site, evaporative emissions from the holding tank are included in this estimate along with stack emissions from vapor treatment. The total emissions represent less than 1% of the amount of contaminants removed from the soil. The removal efficiency for the total mass of contaminants present at the site was not demonstrated, nor was the associated control efficiency.

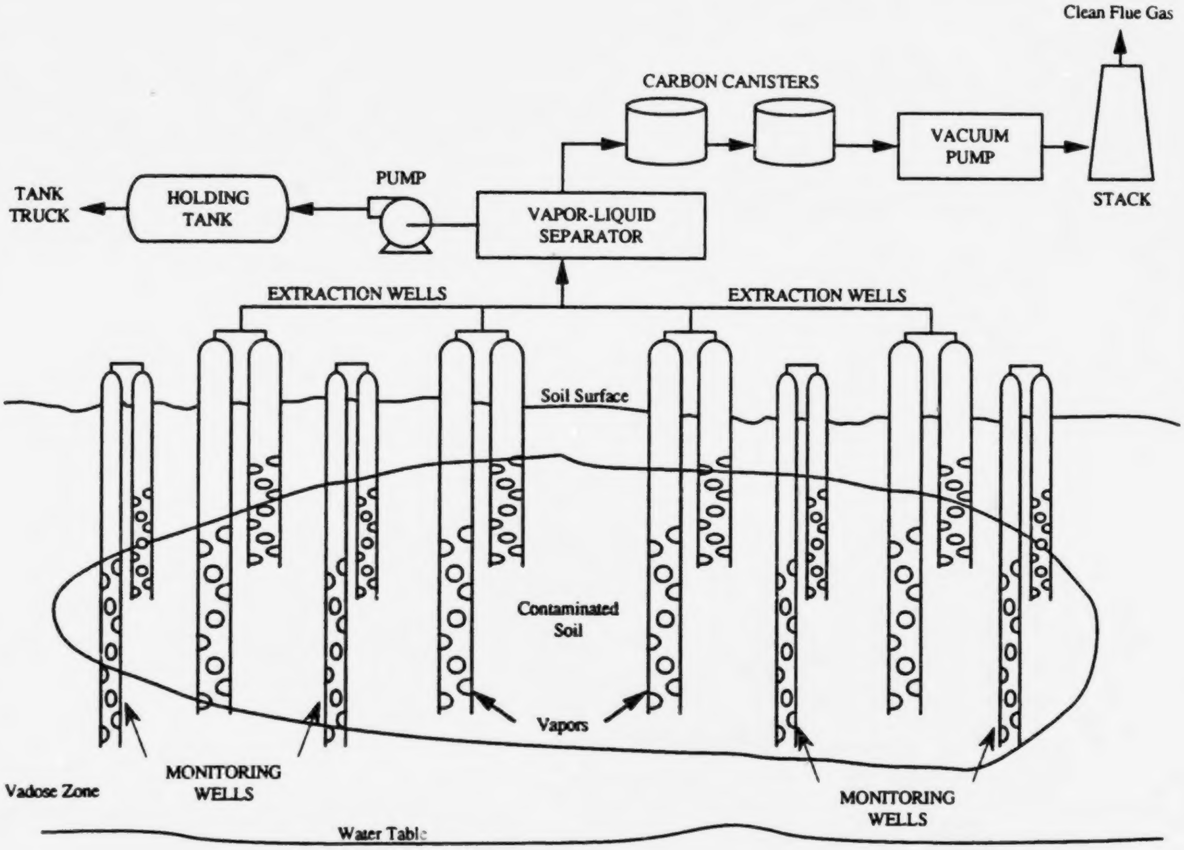
Clean Flue Gas
CARBON CANISTERS
VACUUM PUMP
STACK
TANK TRUCK
HOLDING TANK
PUMP
VAPOR-LIQUID SEPARATOR
EXTRACTION WELLS
EXTRACTION WELLS
Soil Surface
Contaminated Soil
Vapors
MONITORING WELLS
MONITORING WELLS
Vadose Zone
Water Table

Figure 5-3. Process Flow Diagram for Terra Vac In Situ Vacuum Extraction System.

Table 5-3.

Estimated Emissions for Terra-Vac's In-Situ Vacuum Extraction System

Pollutant	Molecular Weight g/mol	Peak Uncontrolled Stack Emissions g/hr[a]	Peak Controlled Stack Emissions g/hr[b]	Evaporative Emissions g/hr[c]	Total Emissions g/hr[d]
TCE	131.29	5,210.0	5.91	3.29	9.20
DCE	96.94	274.0	0.31	0.0	0.31
TRI	133.41	36.0	0.04	0.0	0.04
PCE	165.83	18.0	0.02	0.0	0.02
Totals		5,538.0	6.29	3.29	9.57

[a] Uncontrolled emissions equal removal rate of each contaminant.

[b] Based on measured 99.75% overall control efficiency for two carbon adsorption canisters in series.

[c] Estimated evaporative emissions from contaminated water storage.

[d] Total stack and evaporative emissions.

KEY:

TCE	-	trichloroethylene
DCE	-	trans-1,2-dichloroethylene
TRI	-	1,1,1-trichloroethane
PCE	-	tetrachloroethylene

Costs

The equipment fabrication and construction costs were estimated to be $55,000 (in 1991 dollars). The total cost to remove 6,000 tons of VOCs from the site was estimated to be $310,000 or $52 per ton. Of this, costs for activated carbon were $14 per ton and for waste disposal were $8 per ton. Including power and labor costs, the VOC control system represents about one-half of the total remediation cost.

5.10 References

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6.0 IN-SITU BIODEGRADATION

6.1 Process Description

In-situ biodegradation is the term for biological treatment processes that are performed in place and therefore do not require excavation and removal of the contaminated soil. This treatment method includes widely used technologies such as land treatment as well as some emerging technologies that employ subsurface injection of oxygen or nutrients to promote the biodegradation of contaminants.

The main purpose of in-situ treatment is to employ the natural microbiological activity of soil to decompose organic constituents into carbon dioxide and water. Systems that try to enhance this natural biological activity typically use injection wells to provide an oxygen source (such as air, pure oxygen, or hydrogen peroxide) to stimulate aerobic degradation or add nutrients to support the growth of waste-consuming microorganisms. In some cases, microorganisms may be added to the soil that have the ability to metabolize specific contaminants of interest.

It is important to note that in in-situ biotreatment, biodegradation is actually only one of several competing mechanisms. In in-situ processes the contaminants may also be leached, volatilized, undergo chemical degradation, or be adsorbed onto the soil particles. The overall removal achieved by in-situ biotreatment processes represents the combined impact of all of these mechanisms. In addition, field studies (Eklund, et al., 1986) have shown that volatilization may account for the disappearance of the majority of VOCs being treated.

Since volatilization makes a potentially large contribution to the overall removal achieved by most in-situ biotreatment processes, this technology is generally not suitable for remediating sites which are contaminated with volatile fuels or other contaminants, or for remediating sites that are close to sensitive receptors. In-situ biotreatment is best suited for sites in remote locations and sites that are contaminated with less volatile fuels (such as JP-4, JP-5, or diesel fuel).

Like all biotreatment processes, in-situ treatment is not applicable for the remediation of non-biodegradable contaminants such as heavy metals and other inorganic compounds. Some halogenated organic wastes also are not amenable to biotreatment. The applicability of advanced treatment methods, which rely on subsurface injection of oxygen or nutrients, are also highly dependent on the type of soil in which the contamination has occurred. Studies by the Air Force on the remediation of soil contaminated with JP-4 and JP-5 showed that in soils with low-permeability there was reduced delivery of oxygen and nutrients and consequently little biodegradation occurred (Downey and Elliot, 1990).

The use of landtreatment as a remediation technology is expected to decline due to recent regulatory requirements that RCRA landtreatment facilities have no demonstrated migration of contaminants to the surrounding environment.

Figure 6-1 shows a general schematic of an in-situ biodegradation process. As the figure shows injection wells may be installed around the zone of contamination to provide oxygen and nutrients to stimulate biodegradation.

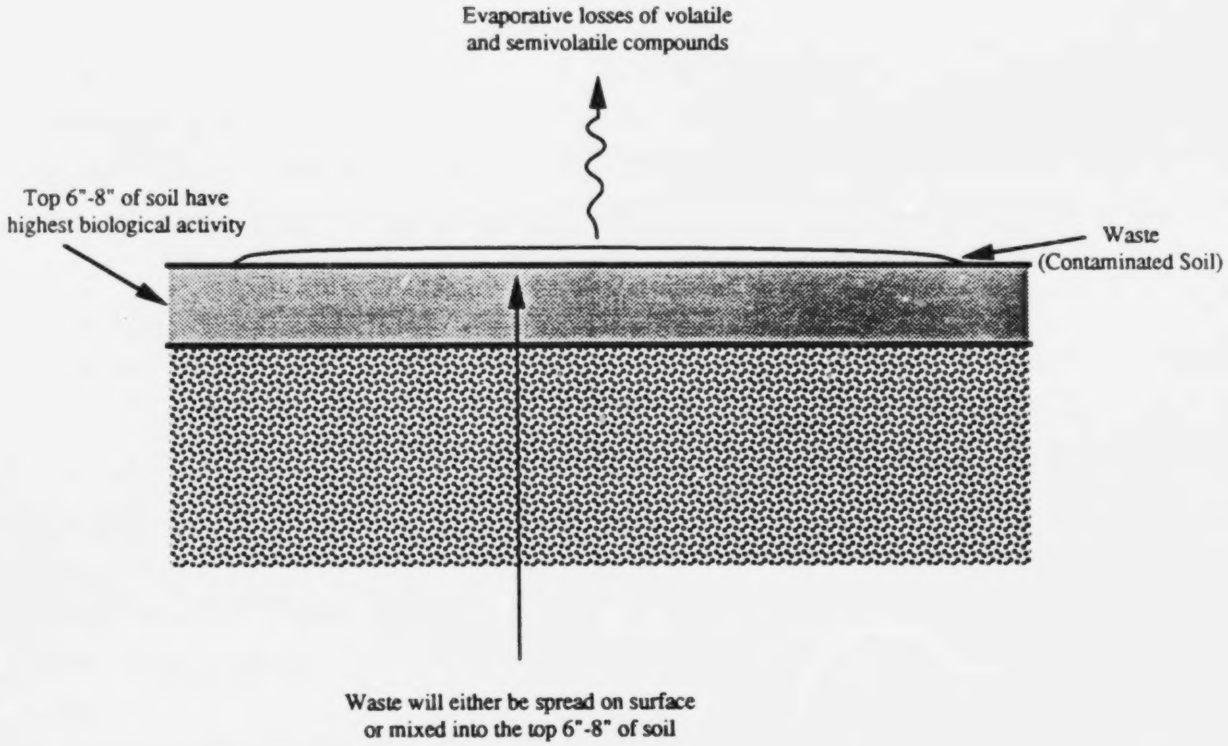
Evaporative losses of volatile
and semivolatile compounds
Top 6"-8" of soil have
highest biological activity
Waste
(Contaminated Soil)
Waste will either be spread on surface
or mixed into the top 6"-8" of soil

Figure 6-1. Generalized Process Flow Diagram for In-Situ Biodegradation.

As suggested in Figure 6-1, the primary advantages of in-situ treatment are simplicity and low-cost. The equipment and operating costs for this type of treatment are very low compared to other technologies. The only heavy equipment that may be required is a disk or rototiller to occasionally expose subsurface soil to the air. However, if typical landtreatment techniques are used to treat the contaminated soil a large area may be required for waste spreading.

In an in-situ biotreatment process, the time required to treat the contaminated soil will vary greatly depending on a number of factors including the:

- Physical and chemical properties of the soil matrix;
- Physical and chemical properties of the contaminant;
- Initial concentration of the contaminant in the soil; and
- Biodegradability of the contaminants (i.e. biodegradation rate constants).

Once the concentration of contaminants in the soil has been lowered either by biodegradation or evaporation, the zone of contamination may be capped or covered with a new soil layer. Field studies of landtreatment have found no evidence of anaerobic decomposition (Eklund, et al, 1986).

6.2 Identification of Air Emission Points

As Figure 6-1 shows, fugitive air emissions from the treated area are the primary waste stream generated in in-situ biodegradation processes. A more localized emission source will exist when and where the waste is applied to the soil (or the contaminated soil pile is being spread). A small amount of additional emissions may also be generated by heavy equipment used to till or move the soil.

6.3 Typical Air Emission Species of Concern

Typical emissions from in-situ biotreatment process are evaporative losses of volatile and semi-volatile organic compounds. If the soil is tilled, though, there also may be some small amounts of paticulate matter (PM) emissions, as well as some combustion emissions if the tilling device is powered by a gas or diesel engine.

The primary environmental factors, in addition to the biodegradability and volatility of the soil contaminants, which influence air emissions are wind speed and temperature. At higher windspeeds the driving force for mass transfer into the gas-phase increases so evaporative emissions tend to be higher. The microorganisms tend to perform best within a narrow temperature range. Deviations from these optimal temperatures (either high or low) will tend to diminish microbial activity and result in slower biodegradation. As a result, competing mechanisms such as volatilization may predominate.

6.4 Summary of Air Emissions Data

Since in-situ biodegradation has not been used in the clean-up of a significant number of fuel spills, there are few data available in the literature on air emissions for this application of in-situ remediation. However, air emissions associated with landtreatment refinery and industrial wastes have been more extensively studied.

Table 6-1 shows the fluxes of volatile organic compound emissions from two plots at a refinery landtreatment facility (Eklund, et al, 1986). The data represent the total emissions per 12 hour period for test plots that were each 423 m^2. As the data show, air emissions from in-situ treatment initially high and decrease as the concentration of volatiles in the soil falls off. Tilling of the soil increased the measured emission fluxes by at least a factor of three. The annual waste loading at this site was

Table 6-1.

VOC Emissions From a Refinery Landtreatment Facility: Average Measured Emission Rates by Plot by Half-Day

Sampling Day	Emission Rate (kg)		
	A-Plot (Surface)	B-Plot (Background)	C-Plot (Sub-surface)
0	1.88	1.48	1.95
1	249	24.7	176
	142	10	52.8
2	22.5	4.09	13.8
	32.6	5.11	26.5
3	48.2	4.09	120
	146	9.93	295
4	33.4	8.18	71.2
	46.3	8.86	67.4
5	16.6	2.71	12.4
	15	6.13	15.1
6	8.04	2.73	10.1
	49.1	10	91.3
7	6.41	2.04	12.1
	13.5	5.8	22
8	21.8	1.32	13
	71.1	--	59.3
9	2.56	2.6	2.93
	7.25	--	5.76
10	1.24	--	3.94
	12.34	1.2	16.2
11	2.49	1.4	11.5
	6.4	1.4	7.13
12	2.97	1.2	4.06
	10.5	4.4	16.2

about 16 L/m^2 of separator float and sludge. Although refinery and industrial wastes may differ significantly from the type of contamination present at a fuel spill, these data may provide an order of magnitude estimate for the emissions that could be expected if in-situ bioremediation were used to treat a fuel spill.

Another field test (Ricardelli cited in U.S. EPA, 1989) demonstrated that approximately 25% of raw oily refinery waste applied to a landtreatment facility was lost to the atmosphere. The author found that compounds with boiling points less than 400°F tended to be volatilized while compounds with boiling points greater than 400°F tended to remain in the soil and be degraded. A third field test (Dupont and Reineman, 1986) measured fluxes of BTXE compounds of up to 0.01 ug/cm^2-sec immediately after application. The measured emission fluxes tended to drop by several orders of magnitude over the first two days after application. Tilling increased the emissions by approximately a factor of two.

Published emission factors for landtreatment are (Thompson, et al, 1991):

Uncontrolled Emissions:

1,500 g/hr (24-hr average)
188 g/hr (20-day average)

6.5 Identification of Applicable Control Technologies

In in-situ bioremediation the area over which air emissions are generated is often quite large. Consequently, it is impossible to apply traditional "end-of-pipe" VOC control technologies to this type of process. General approaches for controlling VOC emissions from area sources such as emission-controlling foams and impermeable covers are discussed in Section 8 on excavation. These approaches, however, are not applicable to in-situ bioremediation since the controls are designed to inhibit the transfer of gases between the soil and the atmosphere. While this reduces VOC emissions, it will also limit the replenishment of oxygen to the soil and may cause anaerobic conditions to develop. Other control approaches such as wind barriers tend not to be applicable for in-situ biotreatment because of the large treatment areas.

One VOC reduction/control approach that is specific for in-situ biotreatment is subsurface injection of waste. It is applicable for liquid wastes, but not for contaminated soil. In this operating practice, a tank truck containing the liquid waste is driven across the treatment area and the waste is introduced into the soil at a depth of 6-12 inches below groundlevel via a series of hollow tines on a tilling device pulled behind the truck. Some researchers have claimed that sub-surface injection can reduce emissions 80% or more over a 24-hour average (Coover, 1990). However, other researchers contend that over a longer period subsurface injection provides only a minor reduction in emissions, especially if the soil if the soil is tilled frequently for aeration (Wetherold, et al, 1985).

6.6 Costs for Remediation

Costs to use traditional land-farming techniques to treat fuel contaminated soil are very low. The only capital requirements are excavating and tilling equipment. Operating requirements are also minimal; only fuel for the heavy equipment and labor may be required to complete the remediation. The total costs for remediating a site are likely to be on the order of $100,000, excluding the cost of any land which much be purchased (Newton, 1990). Assuming 10,000 tons of soil, this would be less than $100/ton.

If some type of advanced in-situ remediation process is applied, e.g. one using oxygen or nutrient addition, clean-up costs may be significantly higher. Table 6-2 (U.S. EPA, 1987) shows estimated site cleanup costs for hypothetical sites at which hydrogen peroxide is used for the enhancement of in-situ biodegradation. The cleanup of 300 gallons of gasoline from a sand/gravel aquifer (Site A) over a period of 6 to 9

Table 6-2.

Estimated Costs for Remediations Using Hydrogen Peroxide to Enhance Biodegradation

	Site A	Site B	Site C
Contaminant	300 gallons of gasoline	2,000 gallons diesel fuel	10,000 gallons jet fuel
Formation	Sand/Gravel	Bedrock	Fine Gravel
Flow Rate	50 gal/min	10 gal/min	100 gal/min
Project Time	6-9 months	9-12 months	14-18 months
Estimated Cost	$92,000 - $157,000	$209,000 - $328,000	$525,000 - $786,000

months is estimated to cost $92,000 to $157,000. Cleanup of 2,000 gallons of diesel fuel from a fractured bedrock formation (Site B) is estimated to require 9 to 12 months and cost $209,000 to $328,000. The cost estimate for degrading 10,000 gallons of jet fuel from a fine gravel formation is estimated to cost $525,000 to $786,000 and take 14 to 18 months.

6.7 Costs For Emissions Controls

The cost for using subsurface injection of the waste soil instead of the traditional surface application is likely small, on the order of $10,000 to 20,000 for application equipment and additional labor.

6.8 Equations and Models For Estimating VOC Emissions

Vapor transport and biodegradation in contaminated soil are complex and competing processes. A PC-based model called LAND7 or CHEMDAT7 (U.S. EPA, 1989) is currently recommended by the EPA to predict the VOC emission rates resulting from the land treatment of wastes. It is a user-friendly program and a user's manual accompanies the software[1]. The model predictions have been compared with available measurement data and have shown a reasonable agreement with the measurement data (U.S. EPA, 1989). The model is expected to be accurate to within an order of magnitude in most cases. Sensitivity studies done using this model under typical conditions has shown the model predicts that 35-80% of the applied volatiles will be emitted to the air and the remainder degraded (Coover, 1989). Evaluations of the Thibodeaux model (also applicable to the LAND7 model) have found it to require significant amounts of input data about the site and the contamination that is present (U.S. EPA, 1989). Values for the input parameters may need to be assumed in many cases; however, default values are available as part of LAND7.

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[1] Can be obtained by calling EPA's Control Technology Center Hotline at 919/541-0800.

6.9 Case Study

As noted previously, traditional landtreatment techniques are not generally recommended for the remediation of soils contaminated with volatile fuels. For such sites, the air emissions from landtreatment are usually high enough to eliminate it from consideration. Air emissions from advanced in-situ bioremediation processes, though, tend to be lower since the biodegradation is faster, and these types of processes are being increasingly used. However, limited full-scale data are available on the effectiveness on these processes. A recent study by the U.S. Air Force indicates that while pumping air into contaminated soil does improve biodegradation it also increases the rate of at which volatile compounds are stripped from the soil. As a result, the offgas from this type of process will require some sort of treatment as shown in Figure 6-2. In some applications the cost of treating the offgas may be substantial.

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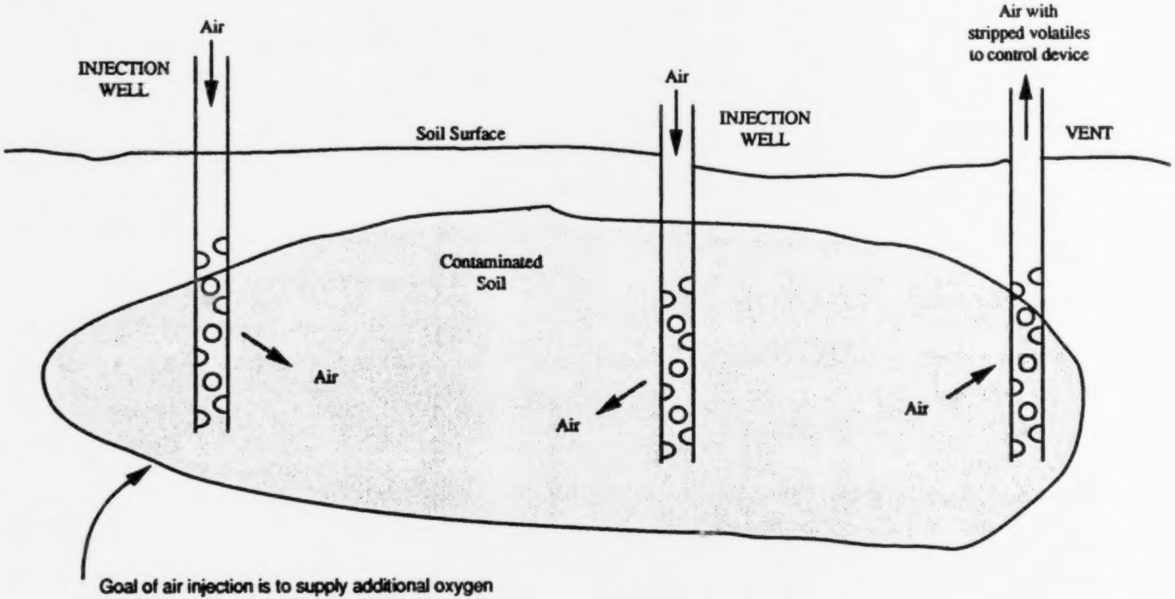

Air
INJECTION WELL
Air
INJECTION WELL
Air with stripped volatiles to control device
VENT
Soil Surface
Contaminated Soil
Air
Air
Air

Goal of air injection is to supply additional oxygen to microbes and speed biodegradation. However, air injection will also strip volatiles from soil.

Figure 6-2. Flow Diagram for Off-Gas Treatment System For In-Situ Biodegradation.

7.0 EX-SITU BIODEGRADATION

7.1 Process Description

Ex-situ biodegradation is the general term for treatment processes in which an aqueous slurry is created by combining soil or sludge with water and then biodegraded in a self-contained reactor or in a lined lagoon. This emerging technology, which is now beginning to move out of the developmental stage, is also referred to as slurry biodegradation.

There are two main objectives behind using slurry bioremediation: to destroy the organic contaminants in the soil or sludge, and, equally important, to reduce the volume of contaminated material. Slurry biodegradation can be the sole treatment technology in a complete cleanup system, or it can be used in conjunction with other biological, chemical and physical treatment.

Slurry biodegradation has been shown to be effective in treating highly contaminated soils that have fuel or other organic contaminant concentrations ranging from 2,500 mg/kg to 250,000 mg/kg. The slurry process has also shown potential for treating a wide range of contaminants including pesticides, creosote, pentachlorophenol, PCBs, and some halogenated organics.

The effectiveness of slurry biodegradation on some general contaminant groups is shown in Table 7-1. This table is based on current available information and engineering judgement (U.S. EPA, 1990).

Figure 7-1 shows a general schematic of the slurry biodegradation process. However, slurry processes may vary significantly among vendors. Each vendor's process may be capable of treating only certain types of contaminants. Treatability studies to determine the biodegradability of the contaminants and the solids/liquid separation that

Table 7-1

Applicability of Slurry Biodegradation for Treatment of Contaminants in Soil, Sediments, and Sludges

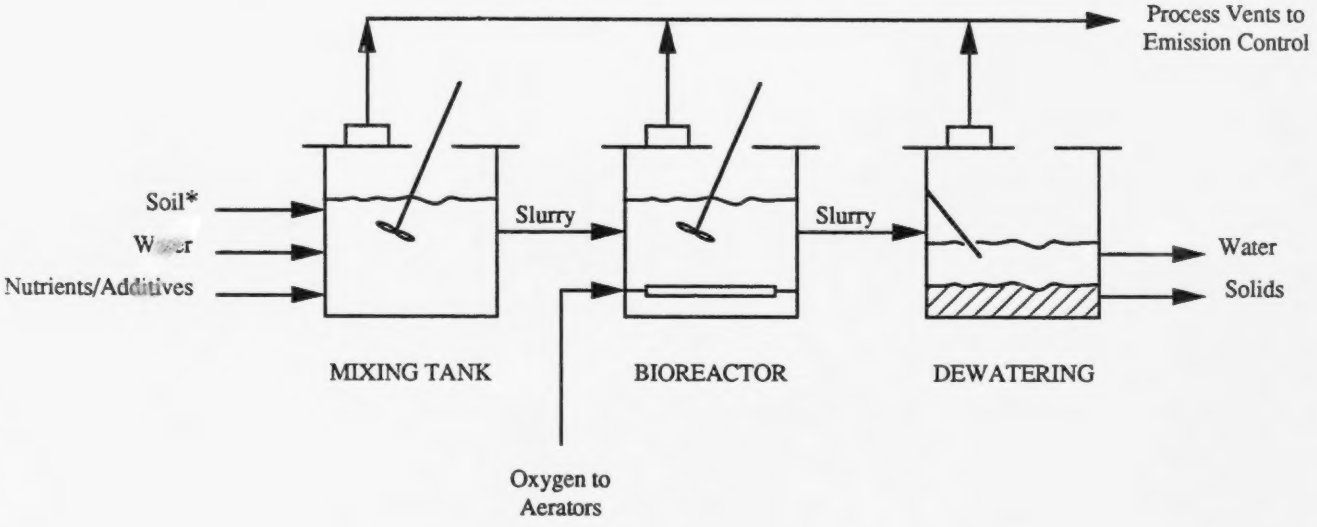
Contaminant	Applicability
ORGANIC CONTAMINANTS:	
Halogenated volatiles	1
Halogenated semivolatiles	2
Nonhalogenated volatiles	1
Nonhalogenated semivolatiles	2
PCBs	1
Pesticides	2
Dioxins/Furans	0
Organic Cyanides	1
Organic Corrosives	0
INORGANIC CONTAMINANTS:	
Volatile metals	0
Nonvolatile metals	0
Asbestos	0
Radioactive materials	0
Inorganic corrosives	0
Inorganic cyanides	1
REACTIVE CONTAMINANTS:	
Oxidizers	0
Reducers	0

KEY:

2 = Demonstrated Effectiveness; Successful treatability test at some scale has been completed.

1 = Potential Effectiveness; Expert opinion is that the technology will work.

0 = No Expected Effectiveness; Expert Opinion is that the technology will not work.


Process Vents to
Emission Control
Soil*
Water
Nutrients/Additives
Slurry
Slurry
Water
Solids
MIXING TANK
BIOREACTOR
DEWATERING
Oxygen to
Aerators

* Waste preparation may be required. This includes excavation as well as other pretreatment to remove metals & other inorganics.

Figure 7-1. Slurry Biodegradation Process Flow Diagram

occurs at the end of the process are typically necessary before final selection of ex-situ biodegradation as a remedy for a given site.

As shown in Figure 7-1, waste preparation is a required first step in applying slurry biodegradation to a contaminated site. The required preparation includes excavation and handling of the waste material as well as screening to remove debris and large objects. Other important waste preparation steps that may be required to meet feed specifications include particle size reduction, water addition, and pH and temperature adjustment. Table 7-2 shows the desired feed characteristics for a typical slurry biodegradation process.

After appropriate pretreatment, the wastes are suspended in a slurry form and mixed in a tank to maximize the contact between contaminants and microorganisms capable of degrading those contaminants. From the mix tank the slurry is pumped (using special slurry pumps) to the bioreactor system. The bioreactor system can either be an above-ground continuously stirred tank reactor (CSTR) or a lined lagoon. Since aerobic treatment is the most common mode of operation for slurry biodegradation, aeration must be provided to the bioreactors by either floating or submerged aerators or by compressors or spargers. Nutrients and neutralizing agents are also supplied to remove any chemical limitations microbial activity. Other materials, such as surfactants and dispersants may be used to improve the material's handling characteristics.

In the bioreactor, microorganisms may be added initially to seed the reaction or added continuously to maintain the correct concentration of biomass. The required residence time for the waste in the bioreactor will depend on a number of factors including:

Table 7-2

Desired Inlet Feed Characteristics for Slurry Biodegradation Processes

Characteristic	Desired Range
Organic Content	0.025 - 25 wt %
Solid Content	10 - 40 wt %
Water Content	60 - 90 wt %
Solids Particle Size	< 1/4 in. diameter
Feed Temperature	15 -35 deg C
Feed pH	4.5 - 8.8

- The physical and chemical properties of the soil or sludge matrix;
- The physical and chemical properties of the contaminant, including its concentration in the waste; and
- The biodegradability of the contaminants.

A typical residence time may be as short as several (e.g. 10) days or as long as 8-9 weeks, depending on site conditions.

Once the biodegradation of the contaminants is completed, the treated slurry is sent to a separation/dewatering system. A clarifier for gravity separation can be used to remove the solid-phase from the soil.

Slurry bioreactors are generally transportable units which can be brought on site by trailer. Typically, commercial units require a set-up area of 0.5-1 acre per million gallons of reactor volume. Water needs at the site can be high since the waste must be put in slurry form. Large quantities of wastewater may also have to be stored on-site prior to discharge to allow time for analytical tests to verify that the discharge standard for the site has been met.

Limited performance data on slurry biodegradation systems are currently available. The data presented in this report are based on information supplied by vendors. The validity of these results has not been evaluated.

Table 7-3 shows performance data for a full-scale slurry biodegradation system, designed by Remediation Technologies, which was used to treat wood preserving sludges at a site in Sweetwater, Tennessee (U.S. EPA, 1990). As the table shows the system achieved an overall removal efficiency of greater than 95%. However, a breakdown of the removal efficiency between biodegradation and volatilization is not available.

Table 7-3

Performance Results for Slurry Biodegradation Process Treating Wood Preserving Wastes[a]

Compounds	Initial Concentration		Final Concentration		Permit Removal[b]	
	Solids (mg/kg)	Slurry (mg/kg)	Solids (mg/kg)	Slurry (mg/kg)	Solids (%)	Slurry (%)
Phenol	14.6	1.4	0.7	< 0.1	95.2	92.8
Pentachlorophenol	687	64	12.3	0.8	98.2	92.8
Naphthalene	3,670	343	23	1.6	99.3	99.5
Phenanthrene & Anthracene	30,700	2,870	200	13.7	99.3	99.5
Fluoranthene	5,470	511	67	4.6	98.8	99.1
Carbazole	1,490	139	4.9	0.3	99.7	99.8

(a) Treatment done using a 50,000 gallon reactor supplied by Remediation Technologies.

(b) Includes the combined effect of volatilization and biodegradation

Another full-scale test of a slurry biodegradation system was recently conducted by ECOVA Corporation (U.S. EPA, 1990). In this cleanup effort more than 750 yd^3 of soil contaminated with pesticides was treated. Soil pesticide levels were reduced from 800 mg/kg to less 20 mg/kg (>97.5% efficiency) in 13 days using a 26,000 gallon bioreactor. Residuals of the process were further treated by land application.

7.2 Identification of Air Emission Points

As Figure 7-1 indicates, there are three primary waste streams generated in slurry biodegradation processes: the treated solids (sludge or soil), the process water, and air emissions. The solids are dewatered and may be further treated if they still contain organic contaminants. Also, if the solids are contaminated with inorganics or heavy metals, they can be stabilized before disposal. Some portion of the process water can be recycled, with the remainder treated in an on-site treatment system prior to discharge.

The air emissions from slurry biodegradation processes can either be area or point sources. For processes using open lagoons, emissions come from the exposed surface of the lagoon. On the other hand in systems using above-ground self-contained reactors, the primary source of emissions is usually a process vent.

7.3 Typical Air Emission Species of Concern

In bioslurry processes the emissions of concern are usually VOCs. The soils handling steps required to deliver the contaminated soil to the treatment unit may also emit significant amounts of VOCs and PM. Emissions from soils handling are addressed elsewhere in this document.

In open lagoons, the primary environmental factors, in addition to the biodegradability and volatility of the waste, which influence air emissions are process temperature and wind speed. Emissions tend to increase with an increase in surface turbulence due to wind or mechanical agitation. Temperature affects emissions through its influence on microbial growth. At temperatures outside the band for optimal microbial activity, volatilization will increase (U.S. EPA, 1989a). Emissions from self-contained reactors are also determined by reactor design parameters such as the amount of air or oxygen used to aerate the slurry. Higher gas flow will strip more volatiles out of solution and increase air emissions.

7.4 Summary of Air Emissions Data

Little information exists on volatile losses from slurry biodegradation processes. Slurry processes have only recently become commercially available and field experience to date is limited. However, data on air emissions from wastewaster biotreatment processes are available. Table 7-4 shows fraction volatilized for different compounds in an industrial aerated wastewaster treatment tank. Although, both the mechanisms for volatilization and biodegradation will be different for the treatment of contaminated soil, this data provides a first estimate of the contribution of volatilization to overall removal for different types of compounds.

7.5 Air Emissions Controls

When the air emissions from slurry biodegradation processes are released through a process vent, standard VOC air pollution control technologies can be applied. Common alternatives for controlling VOC vent emissions include carbon adsorption as well as thermal and catalytic oxidation. Since the vent stream will likely contain only dilute amounts of VOCs, auxiliary fuel must be fired in either thermal or catalytic oxidizers. When the air emissions from slurry biodegradation processes are area air emission sources, applying air pollution control technologies is more difficult. Two control options are commonly used. The first alternative is to use a vapor collection

Table 7-4

Estimated Volatile Losses From Aerated Wastewater Treatment

Compound	Total Mass Loading of Influent Wastewater (g/min)	Estimated Volatile Losses (% of Influent)
Benzene	2.5	0.2
Toluene	1.59	3.5
p,m-Xylene	2.76	0.4
o-Xylene	1.24	0.8
n-Nonane	0.72	21
n-Decane	0.66	20
n-Undecane	0.68	11
Methylcyclohexane	0.64	6.7
Total Non-methane Hydrocarbons	30.1	8.4

hood to capture any VOC emissions and then rout those emissions to a standard control device. A second, generally less favorable, alternative is to use an oil film or foam on top of the slurry to suppress evaporative losses.

Control options for processes with point emission sources are discussed in more detail below. For the relatively low VOC levels and low gas flows from bioreactors, carbon-based VOC emission controls are generally the best choice.

7.5.1 Carbon Adsorption

Carbon adsorption using granular activated carbon (GAC) is the most common control method for vent emissions from processes with dilute VOC containing offgases. In carbon adsorbtion, VOCs are removed by being physically trapped on the surface of the GAC or by chemical reactions with the carbon. The efficiency of GAC is due to its very large surface area per unit mass. Two options for GAC systems are available: 1) "throw away" systems, and 2) fixed bed regenerable systems. In the first option, canisters of GAC are used and disposed of or reactivated off-site. In regenerable systems, steam or hot air is used to strip contaminants from the GAC in place. The contaminants are recovered as a liquid. The cost-effectiveness of regenerable systems will increase as the treatment time and the mass of contaminants to be treated increase.

Modular, skid-mounted treatment systems are available from numerous vendors. Prefabricated GAC units containing up to a ton of carbon are available. Flowrates over 1,000 scfm can be accommodated.

The primary advantage of carbon adsorption over other control options is that the control efficiency of GAC systems is not significantly affected by the changes in air flowrate and VOC concentration. It is applicable to most contaminants having molecular weights between 50 and 150; lighter compounds tend to pass through the GAC unabsorbed and heavier compounds tend to bind permanently to the carbon and cannot be desorbed. GAC tends to be the control method of choice for processes with low VOC concentrations in the exhaust gas (e.g. less than 500-1000 ppmv).

Carbon adsorption has one limitation that may be significant for bioslurry applications. Water vapor will occupy adsorption sites and reduce the removal capacity. It is usually recommended that the gas to be treated have a relative humidity of less than 50% for GAC to be effective. A simple offgas dryer may have to be placed in-line with a GAC unit to be effective treating the emissions from a bioslurry process.

7.5.2 Thermal Incineration

Thermal incineration can be used to destroy vapor-phase contaminants. Contaminant-laden vapors are heated to temperatures above 1000°F via a direct flame or a combustion chamber. The method is applicable to a wide range of compounds and over a large range of concentrations. It is not, however, widely used in applications similar to bioslurry processes. For the flame to be self-sustaining, the VOC concentration needs to be at percent levels that may be above the lower explosive limit for the contaminant of concern. For lower VOC levels, auxillary fuel such as methane or propane must be added. The cost of this fuel can be prohibitive. The efficiency of the method is also affected by changes in the flowrate. As the flowrate varies from design conditions, the mixing and residence times in the incinerator will vary and decrease the destruction efficiency.

7.5.3 Catalytic Oxidation

Catalytic oxidation, also called catalytic incineration, is similar in design and operation to thermal incineration except that a catalyst is present that enhances combustion. The catalyst is usually palladium or platinum in a metallic mesh, ceramic honeycomb, or catalyst-impregnated beads in a packed bed. The catalyst allows destruction to occur at lower temperatures than for thermal incineration (600-900°F). There is therefore less auxillary fuel required and comensurate lower fuel costs.

Design efficiencies of 95 to 99 percent are typical. The catalyst can be damaged by overheating, so the air stream must be diluted, if necessary, to keep the VOC concentration below about 3000 ppmv. Maintenance of this VOC level raises the capital and operating cost of the system since accurate monitoring of the gas stream is needed as is the ability to control the dilution of the gas stream. As for thermal incinerators, catalytic oxidation systems function best when the flowrate is constant.

The catalyst will become less effective over time and can be adversely impacted by trace contaminants in the gas stream. Depending on the type of catalyst employed chlorinated hydrocarbons, mercury, phosphorus, and heavy metals can damage the catalyst.

7.6 Costs for Remediation

Presently there are little cost data available on slurry biodegradation processes because of limited experience with this type of remediation. One vendor estimates the cost of full-scale operation to be \$110-210/m^3 (\$85-160/yd^3) of soil, depending on the initial contaminant concentration and the total amount of soil to be treated. On a mass basis this cost estimate corresponds to \$70-130/ton of contaminated soil. The process cost will also vary depending on the need for additional pre- and post-treatment of the soil and on the type of air emission control equipment.

7.7 Costs for Emissions Controls

Equations for predicting the costs of emission controls based on system design parameters are available (PES, 1989). Section 5 of this document provides typical costs for various types and sizes of treatment systems which could be applied to an ex-situ biodegradation process. As mentioned in Section 5, the cost estimates are drawn from a number of vendors and therefore a range is shown in most cases. The cost data are intended to show the general level of costs likely to be incurred.

7.8 Summary of Existing Air Emissions Data and Models

Although no models have been explicity developed for estimating emissions for ex-situ processes treating contaminated soil, there are currently, several public-domain PC models that are available for estimating air emissions from a variety of other biotreatment options, principally surface impoundments. The two most commonly used models are CHEMDAT-7 (U.S. EPA, 1989b) and the Surface Impoundment Modeling System (SIMS). Both CHEMDAT-7 and SIMS are based on mass transfer and biodegradation models developed by the U.S. EPA. The mass transfer model uses two-film resistance theory, along with the characteristics of the impoundment, to estimate overall mass transfer coefficients for each pollutant. The biodegradation model assumes Monod kinetics to estimate a biodegradation rate.

The accuracy of estimating emissions from ex-situ biotreatment processes, though, is limited by the assumptions inherent in both CHEMDAT-7[1] and SIMS. Both models perform all calculations at 25°C and rely on physical property and kinetic data that are not always readily available for the modeled contaminants. Furthermore, both models rely on a simple thermodynamic analysis and are only valid in the Henry's Law regime. Henry's Law is applicable to dilute solutions and may not be applicable to bioslurries. In addition, neither CHEMDAT-7 nor SIMS use thermodynamic models that can predict the presence of two liquid phases.

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[1] Software and user's guide can be obtained by calling EPA's Control Technology Center Hotline at 919/541-0800.

The validity of CHEMDAT-7 and SIMS for modeling emissions from ex-situ biotreatment processes will depend on the process used and the operating parameters. Their validity must be evaluated on a case-by-case basis. If these models prove to be unacceptable for a given application, emissions can be estimated using a simple mass balance approach. For continuous flow systems, the following correlation is applicable (Thompson, et al., 1991):

$$ER_i = (C_i/1{,}000)(M_r)(\%V_i/100)$$

where:
ER_i = emission rate for contaminant i (g/hr);
C_i = concentration of species i in contaminated soil (mg/kg);
M_r = mass rate of soil treated (kg/hr); and
V_i = percentage of contaminant i volatilized.

The percentage of each contaminant that is volatilized will vary greatly depending on the physical properties of the contaminant and the design of the treatment system. Based on field studies of an aerated impoundment treating contaminated water, as much as 20% of each compound may be volatilized depending on its volatility and biodegradability (Eklund, et al, 1987).

For batch treatment systems a similar expression can be used to estimate air emissions:

$$ER_i = (C_i/1{,}000)(M)(\%V_i/100)/(t)$$

where:
ER_i = emission rate for contaminant i (g/hr);
C_i = concentration of species i in contaminated soil (mg/kg);
M = mass of soil treated (kg);
V_i = percentage of contaminant i volatilized; and
t = residence time in treatment system.

Again volatilization may be 20% or higher depending on the properties of the compound of interest.

Emissions will also occur when excavating the contaminated soil, while transporting it to the treatment unit, during any soil preparation steps, and when feeding the soil into the treatment process. These fugitive emissions are not addressed in either the PC-based models or in the mass balance equations discussed above. Fugitive VOC emissions from soils handling operations are addressed in Section 8.

7.9 References

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8.0 INCINERATION

Information is presented in this section on incineration. The use of incineration to remediate soils contaminated with fuel products is limited and is much less common than the use of thermal desorption, excavation and removal, etc.

8.1 Process Description

A broad range of technologies fall into the category of thermal destruction or incineration. The most common incineration technologies include liquid injection, rotary kiln, and multiple hearth (Lee et al, 1986; Cheremisinoff et al, 1986). However, for remediation of fuel-contaminated soils, rotary kilns are most often used. In general, soil remediation by thermal destruction fall into two general categories: 1) on-site treatment using a transportable incinerator, or 2) off-site treatment where contaminated soils are shipped to a larger, permanent unit. For the treatment of soils contaminated with petroleum fuels, on-site incineration using mobile or transportable units is much more common than off-site incineration. Although incineration is a well-established technology, the evolution of mobile or transportable incinerators is a relatively new development. The literature on incineration is very extensive. The best sources of information on air emissions from incineration are two recent reviews (Oppelt, 1987) and (Eklund, et al., 1989). The Oppelt article is contained in Appendix F to this report.

In broad terms, thermal destruction of hazardous waste is an engineered process in which controlled combustion is used to reduce the volume of an organic waste material and render it environmentally safe. Thermal treatment is a flexible process capable of being used for many waste types including solids, gases, liquids, and sludges. The advantages of thermal treatment include the following:

- Demonstrated effectiveness;
- Applicability to a wide range of wastes (can be used on most contaminant and soil types); and
- High commercial availability.

However, thermal treatment also has a number of significant disadvantages such as:

- High cost;
- Public resistance to the construction and permitting of incinerators; and
- The need to meet stringent treatment requirements for process residuals.

Figure 8-1 shows a generalized process flow diagram for thermal treatment systems. A typical system includes the waste feed system, primary and (in most cases) secondary combustion chambers, and exhaust gas conditioning system.

At the front-end of a hazardous waste incineration system is the waste feed process. The configuration of the waste feed system is determined by the physical characteristics of the waste. Contaminated soil is introduced to the combustion chamber by means of screw augers or belt feeders. If liquids are to be treated as well in the incinerator, they are usually injected into the unit by means of an atomization nozzle(s) which uses steam or compressed air as an atomization fluid. Liquids with entrained solids may require screening to prevent clogging of the atomizer nozzle.

The largest part of the waste destruction usually takes place in the primary combustion chamber. As mentioned earlier, for contaminated soils this chamber is usually a rotating kiln. Gases formed in the primary combustion chamber are then routed to a secondary combustion chamber, or afterburner, where any unburned hydrocarbons or products of incomplete combustion such as CO can be fully oxidized.

After the combustion gases leave the incinerator, they may be routed through a variety of air pollution control devices including gas conditioning, particulate removal, and acid gas removal units. Gas conditioning is accomplished with equipment such as waste heat boilers or quench units. Typical particulate removal devices include venturi scrubbers, wet electrostatic precipitators, ionizing wet scrubbers, and fabric filters.

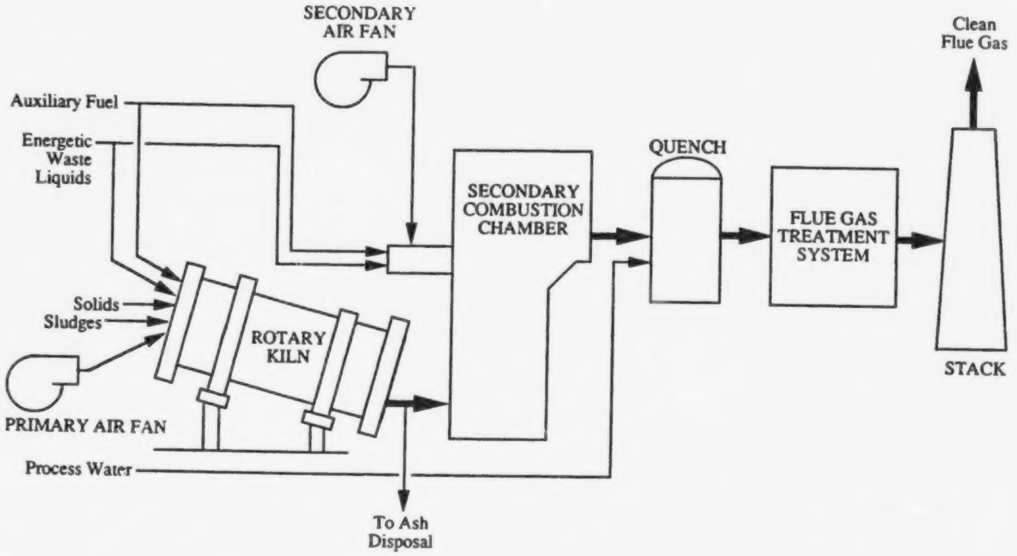
SECONDARY AIR FAN
Clean Flue Gas
Auxiliary Fuel
Energetic Waste Liquids
QUENCH
SECONDARY COMBUSTION CHAMBER
FLUE GAS TREATMENT SYSTEM
Solids
Sludges
ROTARY KILN
STACK
PRIMARY AIR FAN
Process Water
To Ash Disposal

Figure 8-1. Process Flow Diagram for Commercial Rotary Kiln Incinerator

Acid gas removal units include packed, spray, or tray tower absorbers; ionizing wet scrubbers; and wet electrostatic precipitators.

8.2 Identification of Air Emission Points

The air emissions associated with full-scale thermal treatment are primarily stack emissions of combustion gas. There may, however, be some additional evaporative emissions from equipment leaks and waste handling. Full-scale, off-site incineration units may vent all emissions from waste handling and transfer activities to the combustion chamber as make-up air. The air emissions for on-site incinerators are similar to off-site units, except that waste handling activities have a greater likelihood of being uncontrolled. For off-site units, typical incinerator stacks will be 100-200 ft high. For transportable units stack heights may be in the range 40-100 ft. The fugitive emissions sources associated with thermal treatment will likely be ground-level.

8.3 Typical Air Emission Species of Concern

Emissions from both on-site and off-site incinerators include: undestroyed organics, metals, particulate matter, nitrogen oxides (NO_x), carbon monoxide (CO), and acid gases. The cause of each of these pollutants is discussed below. Fugitive emissions associated with excavation, storage, and handling of the feed material must also be considered when assessing potential air impacts from incineration (see Section 8).

Unburned Hydrocarbons

In general, incinerators treating wastes must achieve a required destruction and removal efficiency of at least 99.99% for RCRA wastes and 99.9999% for PCB- or dioxin surrogate wastes. The remaining 0.01% or 0.0001% of the waste can be assumed to pass through the system uncombusted (Eklund, et al., 1989). However, in addition to unburned hydrocarbons there may be some additional reactions in the combustion process that may produce a number of simpler organic compounds, called products of incomplete combustion (PICs). PICs may include dioxin, formaldehyde, and benzo(a)-

pyrene and other polynuclear aromatic hydrocarbons. PIC formation is not restricted to the combustion chamber; the reactions which produce PICs may continue to occur in the combustion gases as they travel through the incineration system and out the exhaust gas (Eklund, et al., 1989; Treholm and Oberacker, 1985).

Studies indicate that PIC emissions are a natural consequence of the kinetically-limited thermal degradation of hazardous wastes. Comparison of PIC formation/destruction rates based on theory and nominal incineration conditions indicate that PIC emissions can be several orders of magnitude higher than predicted based on equilibrium (Dellinger, et al., 1991). This suggests that temporal or spatial excursions from these nominal conditions are occurring that lead to PIC formation. Possible causes of PIC emissions include low temperatures due to quenching, residence time short circuits due to nonplug flow and/or unswept recesses, and locally high waste/oxygen concentration ratios due to poor microscale mixing.

Metals

The metals introduced to the incinerator via the waste feed stream are not destroyed. Depending on their boiling point, they can either be volatilized or remain as solids. Volatilized metals will exit the stack as a gas or they will condense or adsorb onto particles in the stack gas stream. Metals associated with particulate matter (PM) will be captured in the PM control device. Non-volatilized metals can be fluidized and swept up into the combustion gas or leave the incinerator in the bottom ash.

Particulate Matter

The waste feed, auxiliary fuel, and combustion air can all serve as sources for particulate emissions from an incineration system. Particulate emissions may result from inorganic salts and metals which either pass through the system as solids or vaporize in the combustion chamber and recondense as solid particles in the stack gas. High molecular weight hydrocarbons may also contribute to particulate emissions if oxidation is not complete. RCRA requirements for particulate emissions call for a limit of 0.08 grains/dscf corrected to 7% O_2. A number of potential PM control devices can be used, including venturis, wet ESPs, ionizing wet scrubbers, and fabric filters.

Nitrogen Oxides

Achieving high levels of destruction of organic wastes is directly related to combustion chamber temperature: the higher the temperature, the greater the DRE of organics. Unfortunately, the fixation of nitrogen and oxygen to form NO_x also increases with combustion temperatures. NO_x emissions caused by this mechanism are referred to as thermal NO_x. Also if there are bound nitrogen atoms in the waste (e.g. amines), additional NO_x emissions, called fuel NO_x, will be formed. In such cases, two stage combustion or emissions controls may be needed.

Carbon Monoxide

Carbon monoxide emissions are generally low (<100 ppmv) in incinerators due to the high operating temperatures and excess oxygen maintained in the process.

Acid Gases

Hazardous waste incineration will also produce acid gases. These include oxides of sulfur (SO_x), and halogen acids (HCl, HF, and HBr). The sulfur, chlorine, fluorine, and bromine contents of the waste and fuel feed determine the emission levels of their respective acid gases. The concentrations of these elements range widely amongst different wastes; consequently, the resulting acid gas emissions will also show wide variability. Acid gas emissions will usually not be a concern for the incineration of soils contaminated by petroleum fuels. Most incinerators will be equipped with some type of flue gas treatment system to control acid gas emissions. Control efficiencies will typically range from 85-99%. Units treating soil contaminated with halogenated solvents will generally be required to meet RCRA requirements governing HCl emissions.

8.4 Summary of Air Emissions Data

The wide variety in design and operation of incinerators makes it difficult to generalize about air emissions. However, extensive research has been done to determine the range of unburned hydrocarbon and PIC emissions that can be expected from full-scale incinerators. Table 8-1 shows the range of PIC concentrations found in testing of several different full-scale incinerators. Given the volume flowrate of the incinerator offgas these concentrations can be used to estimate the range of emissions from a particular incinerator system. The data in Table 8-1 are not necessarily based on the incineration of fuel contaminated soils, and therefore, may overestimate emissions from the treatment of fuel contaminated soils.

8.5 Identification of Applicable Control Technologies

Unlike other soil remediation technologies, incineration, which converts organics into carbon dioxide and water, does not require additional add-on VOC controls. However, additional controls are usually required to reduce emissions of acid gases, particulate matter (PM), and metals.

The two primary alternatives for controlling acid gas and PM emissions are wet or dry scrubbing systems. Wet scrubbing systems typically use a packed- or spray-tower scrubber with a caustic scrubbing solution to remove acid gases and a venturi scrubber or wet electrostatic precipitator to remove particulate matter. Dry scrubbing systems typically use a spray dryer absorber or dry sorbent injection to remove acid gases from the waste gas stream. The calcium-based alkali absorbent is usually in the form of slaked lime. Semi-dry systems inject the alkali as a slurry with water which is then evaporated off. Dry ESPs or fabric filters are used to remove particulate matter from the gas stream. Table 8-2 shows typical ranges of emissions and estimated removal efficiencies for acid gas and PM control systems. The efficiency of PM control systems will depend on the particle size range present in the flue gas.

Table 8-1.

PICs Found in Stack Effluents of Full-Scale Incinerators[1]

PIC	Number of Sites	Concentrations (ng/L)
Benzene	6	12 - 670
Chloroform	5	1 - 1,330
Bromodichloromethane	4	3 - 32
Dibromochloromethane	4	1 - 12
Bromoform	3	0.2 - 24
Naphthalene	3	5 - 100
Chlorobenzene	3	1 - 10
Tetrachloroethylene	3	0.1 - 2.5
1,1,1-Trichloroethane	3	0.1 - 1.5
Hexachlorobenzene	2	0.5 - 7
Methylene chloride	2	2 - 27
o-Nitrophenol	2	25 - 50
Phenol	2	4 - 22
Toluene	2	2 - 75
Bromochloromethane	1	14
Carbon disulfide	1	32
Methylene bromide	1	18
2,4,6-Trichlorophenol	1	110
Bromomethane	1	1
Chloromethane	1	3
Pyrene	1	1
Fluoranthene	1	1
Dichlorobenzene	1	2 - 4
Trichlorobenzene	1	7
Methyl ethyl ketone	1	3
Diethyl phthalate	1	7
o-Chlorophenol	1	2 - 22
Pentachlorophenol	1	6
2,4-Dimethyl phenol	1	1 - 21

[1] Data from Trenholm, Gorman, and Jungclaus, 1984.

Table 8-2.

Characteristics of Off-Gas from On-Site Incineration Systems

Table 8-2a. Typical Properties of Off-Gas from Combustion Chamber[a]

Parameter	Units	Value
Air flow rate	ACFM	30,000 - 50,000
Temperature of Exit Gas	°F	1,400 - 1,800
Oxygen Content	%	3
System Pressure Drop	In. H_2O	10 - 15

[a]Based on a limited number of designs

Table 8-2b. Typical Emissions

	EPA* Conservative Estimated Efficiencies	Typical Actual Control Efficiencies	Typical Range of Emission Rates
Particulate Matter	99+%	99.9+%	0.005-0.02 gr/dscf
Hydrogen chloride (HCl)	--	99+	10-50 mg/Nm^3
Sulfur dioxide (SO_2)	--	95+	30-60
Sulfuric acid (H_2SO_4)	--	99+	2.6
Arsenic	95	99.9+	1-5 μg/Nm^3
Beryllium	99	99.9	<0.01-0.1
Cadmium	95	99.7	0.1-5
Chromium	99	99.5	2-10
Antimony	95	99.5	20-50
Barium	99	99.9	10-25
Lead	95	99.8	10-100
Mercury	85 - 90	40 - 90+	10-200
Silver	99	99.9+	1-10
Thallium	95	99+	10-100
PCDD/PCDF**	--	90-99+	1-5 ng/Nm^3

*Based on spray dryer fabric filter system or 4-field electrostatic precipitator followed by a wet scrubber.

** Total all cogeners.

SOURCE: Donnely, 1991.

8.6 Costs for Remediation

The costs to use thermal destruction to remediate fuel-contaminated soil will, of course, vary from site to site and depend on whether on-site or off-site treatment is used. The choice between off-site and on-site incineration is usually determined by the volume of soil to be treated and the proximity of full-scale off-site hazardous waste incinerators. The cost of using a transportable on-site incinerator will only be justified if the volume of contaminated soil to be remediated is large and/or the expense of off-site incineration is excessive because of transportation costs or other factors.

Table 8-3 shows approximate costs for off-site incineration. As the table shows the estimated cost for incinerating contaminated soil is \$540 - \$1,070 per ton including transportation costs. It should be emphasized that this costs will vary with type of contamination and the volume of soil to be remediated (Cochran, R., et al., 1987).

Table 8-4 shows approximate costs for on-site incineration (U.S. EPA 1990). As indicated in the table, costs may range from \$180 to \$1,580 per ton depending on the volume of soil being remediated. Also, as the table shows, on-site incineration is most economical when a large volume of waste must be treated. The cost of remediation per ton falls significantly as the volume increases. For large-scale on-site incineration, capital costs are on the order of 5 to 15 millon dollars. Operating costs which consist primarily of fuel and labor will also be substantial. Additional costs will also be incurred for the disposal of the incinerator ash, unless the treated soil can be backfilled on-site.

Table 8-3.

Estimated Range of Costs for Off-Site Incineration[a]

Types of Waste	Cost Range ($/ton)	
Drummed Waste	$170	$540
Liquids	$70	$540
Clean Liquids with High Btu Value	$20	$70
Soils and/or Highly Toxic Liquids	$540	$1,070

[a] Data from Cochran, R., et al., 1987.

Table 8-4.

Estimated Range of Costs for On-Site Incineration[a]

Site Size (Tons)	Cost Range ($/ton)	
Very Small (<5,000)	$530	$1,580
Small (5,000 - 15,000)	$390	$1,020
Medium (15,000 - 30,000)	$260	$680
Large (>30,000)	$180	$530

[a] Data from Engineering Bulletin: Mobile/Transportable Incineration Treatment (U.S. EPA/540/2-90-014) 1990. Data are for the treatment of hazardous waste.

8.7 Costs for Emissions Controls

Costs for controlling acid gas and particulate emissions are substantial. Depending on the volume gas treated, the installed cost for a wet scrubbing system on a full-scale (i.e. fixed base) incinerator could be $1,000,000-$3,000,000. Costs for wet scrubber controls for a mobile system are likely to be on the order of $200,000-$1,000,000. Similar costs would be expected for dry scrubbing systems.

8.8 Equations and Models for Estimating VOC Emissions

A simple mass approach (Thompson et al, 1991) can be used to estimate emissions from incineration. Separate correlations for each pollutant of concern are presented below.

Unburned Hydrocarbons

An emission rate for unburned hydrocarbons can be generated from a mass balance on the incinerator system:

$$ER_i = (1-(DRE_i/100))(C_i)(m_w)$$

where:
ER_i = emission rate for pollutant i (g/hr);
DRE_i = destruction efficiency (assume 99.99% if not known);
m_w = total mass flow rate of waste feed (kg/hr); and
C_i = waste feed concentration for pollutant i (g/kg).

Products of Incomplete Combustion

Emissions of PICs, both the amount and the type, will vary greatly from unit to unit depending on design and waste feed. Data is currently unavailable to generate a single emission factor.

Metals

Metals are not destroyed in the incineration process. They leave the system via either the bottom ash, are captured in the air pollution control system, or exit with the stack gas. There are currently no correlations available for determining the partitioning of metal emissions in incineration systems. If stack data is available for the incinerator in question, metals emissions rates can be estimated from:

$$ER_i = (C_i)(m_w)(\%ME_i/100)$$

where: ER_i = emission rate for metal i (g/hr);
C_i = concentration of metal i in the feed (g/kg);
m_w = mass flow rate of waste (kg/hr); and
$\% ME_i$ = metal emitted to air expressed as a percentage of metal fed (See EPA, 1989).

Acid Gases

The production of acid gases (HCl, SO_2, and HF) is determined by the respective chlorine, sulfur, and fluorine contents in the waste and fuel feed streams. A conservative approach to calculating the air emissions of these acid gases is to assume complete conversion of Cl, S, and F into their respective acid gas products and apply a typical removal efficiency for the air pollution control system. These equations follow the form:

$$ER_i = (Cj)(R_{i/j})m_w(1-\%CE_i/100)$$

where ER_i = emission rate for acid gas i (g/hr);
C_j = concentration of element (Cl, S, or F) in waste (g/kg);
$R_{i/j}$ = stoichiometric ratio of acid gas to element (kg/kg);
m_w = mass flow rate of waste (kg/hr); and
$\%CE_i$ = control efficiency of acid gas treatment system.

Nitrogen Oxides and Carbon Monoxide

In general, incinerator systems are not considered significant sources of NO_x emissions. NO_x is usually only a concern for wastes with high nitrogen content. Typical NO_x emissions for an incinerator may be on the order of 100-200 ppmv (dry basis), or expressed on a fuel basis, 0.12-0.33 lbs NO_x per MMBtu. If a low-NO_x burner is used, the emissions may be on the order of 0.05 lbs of NO_x per MMBtu.

CO emissions from incinerators are also not considered a major problem. Most systems are designed to be fired with excess air (i.e. oxygen rich) to ensure complete combustion of organic material to carbon dioxide. Vendors typically guarantee CO emissions less than 100 ppmv (dry basis). Actual measured CO levels are often lower.

8.9 Case Study: On-Site Incineration

No suitable case study was found for the incineration of soils contaminated with petroleum fuels.

8.10 References

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9.0 SOIL WASHING/SOLVENT EXTRACTION

9.1 Process Description

Three remediation technologies are described below: soil washing, solvent extraction, and soil flushing. These are all primarily separation processes and further treatment of the collected contaminants will typically be required.

9.1.1 Soil Washing

Soil washing is an *ex situ* process in which contaminated soil is excavated and fed through a water-based washing process. It operates on the principle that contaminants can be dissolved or suspended in an aqueous solution or removed by separating out clay and silt particles and the associated adhered contaminants from the bulk soil. The aqueous solution containing contaminants may be treated by conventional wastewater treatment methods (U.S. EPA, 1990a).

Most organic and inorganic contaminants bind chemically or physically to clay or silt soil particles, which in turn adhere to larger sand and gravel particles primarily by compaction and adhesion. Particle size separation by washing enables the contaminated clay and silt particles (and the bound contaminants) to be concentrated. Separating the sand and gravel from the small contaminated soil particles significantly reduces the volume of contaminated soil, making further treatment or disposal much easier. The larger particles may be returned to the site (U. S. EPA, 1990b).

If soil washing lowers contaminant concentrations in the soil to acceptable levels, the only additional treatment to consider would be emissions controls. Soil washing also serves as a cost-effective pre-processing step for further treatment. It can potentially be effective for the remediation of soils with a small amount of clay and silt particles and with a wide variety of organic, inorganic, and reactive contaminants. Large amounts of clay and silt particles mitigate the effectiveness of soil washing and make it inadequate as the only treatment method. Removal efficiencies range from 90-99 percent for volatile organic compounds (VOCs) and 40-90 percent for semi-volative compounds. Compounds with low water solubilities such as metals and pesticides sometimes require acids or chelating agents to assist in removal (U.S. EPA, 1990a).

Particle size distribution is a key parameter in determining the feasibility of soil washing. The relative effectiveness of soil washing for various soil types are shown below.

Particle size distribution	Effectiveness
>2mm	Oversize pretreatment requirements
0.25-2 mm	Effective soil washin
0.063-0.25 mm	Limited soil washing
<0.063 mm	Clay and silt fraction: difficult soil washing

Bench-scale and pilot-scale treatability tests are recommended before undertaking full-scale operation. Further concerns about feasibility include the fraction of hydrophobic contaminants that require surfactants or organic solvents for effective removal, the complexity and stability of the contamination that affect washing fluid formulation, and the effect of washwater additives on wastewater treatment (U.S. EPA, 1990a).

Excavation and removal of debris and large objects precedes the soil washing process. Sometimes water is added to the soil to form a slurry that can be pumped. After the soil is prepared for soil washing, it is mixed with washwater and sometimes extraction agents. At this point, three separation processes occur: 1) water-soluble contaminants are transferred to the washwater; 2) contaminants are suspended in the washwater; and 3) clay and silt particles to which contaminants are adhered separate from larger soil particles. After separation from the washwater, the soil is rinsed with clean water and may be returned to the site. The suspended soil particles are removed by gravity from the washwater as sludge. Sometimes flocculation is used to aid in sludge removal. This sludge is more highly contaminated than the original soil and undergoes further treatment or secure disposal. The spent washwater from which the sludge is removed is treated and recycled. Residual solids from the recycle process may require further treatment (U.S. EPA, 1990a).

Soil washing generates four waste streams:

1) contaminated solids separated from the washwater;
2) wastewater
3) wastewater treatment sludges and residual solids; and
4) air emissions.

Any of a number of treatments is feasible for the contaminated clay fines and solids. They may successfully undergo incineration, low temperature thermal desorption, solidification and stabilization, and biological or chemical treatment. It is recommended that as much blowdown water be recycled as possible. Blowdown water released to local wastewater treatment plants must meet local discharge standards. Sludges and solids from wastewater treatment require appropriate treatment and disposal. Collected air emissions from the waste site or soil washing unit can be treated as well (U.S. EPA, 1990a).

Advantages of the soil washing process include:

1) applicability to a wide variety of organic and inorganic compounds.
2) high removal efficiencies for certain soil types; and
3) minimal fire and explosion hazards.

Some disadvantages as compared to other remediation processes are that soil washing:

1) is suitable for only certain soil types;

2) does not destroy contaminants; and

3) may require additives that improve removal but compromise treatment of the waste streams.

Figure 9-1 shows a process diagram of the soil washing process.

9.1.2 Solvent Extraction

Solvent extraction differs from soil washing in that it employs organic solvents rather than aqueous solutions to extract contaminants from the soil. Like soil washing, it is a separation process that does not destroy the contaminants. The contaminants will have greater solubility in the solvent than in the soil. The equilibrium concentration gradient drives the mass transport process such that the contaminant transfers from the soil to the solvent. When the soil is separated from the solvent, the soil contaminant concentrations are presumably lower than before contact with the solvent. Soil washing treats organic compounds much more effectively than inorganic compounds and metals. It can be used in conjunction with other processes to reduce remediation costs (U.S. EPA, 1990b).

Sediments, sludges, and soils contaminated with volatile organic compounds (VOCs), polychlorinated biphenyls (PCBs), halogenated solvents, and petroleum wastes can be effectively treated with solvent extraction. The removal of inorganic compounds such as acids, bases, salts, and heavy metals is limited, but the compounds usually do not hinder the remediation process. Metals may undergo a chemical change to a less toxic or leachable form but their presence in the waste streams may also restrict disposal and recycle options (U.S. EPA, 1990b).

The remediation process begins with excavating the contaminated soil and feeding it through a screen to remove large objects. In some cases, solvent or water is added to the waste in order to pump it to the extraction unit. In the extractor, solvent is added and mixed with the waste to promote dissolving of the contaminants into the solvent. Laboratory testing can determine which solvent adequately separates the contaminants from the soil. Generally, the solvent has a higher vapor pressure than the

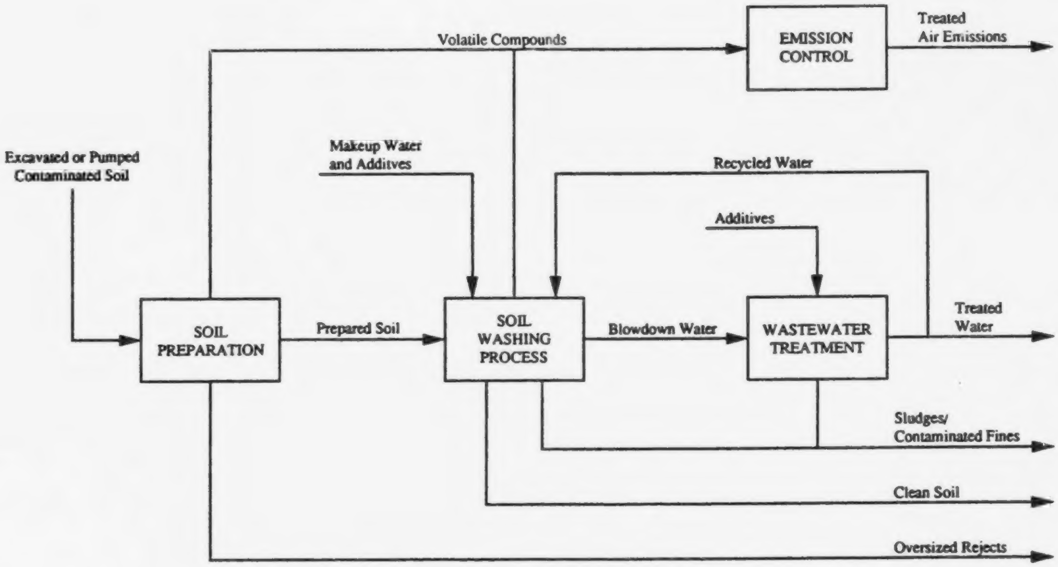
Volatile Compounds
EMISSION CONTROL
Treated Air Emissions
Excavated or Pumped Contaminated Soil
Makeup Water and Additives
Recycled Water
Additives
SOIL PREPARATION
Prepared Soil
SOIL WASHING PROCESS
Blowdown Water
WASTEWATER TREATMENT
Treated Water
Sludges/ Contaminated Fines
Clean Soil
Oversized Rejects

Figure 9-1. Schematic Diagram of Aqueous Soil Washing Process

contaminants so that with an appropriate pressure or temperature change, the solvent may be separated from the contaminants, compressed, and recycled to the extractor (U.S. EPA, 1990b).

Up to five waste streams may result from the solvent extraction process:

1) Concentrated contaminants;
2) Solids;
3) Wastewater;
4) Oversized rejects; and
5) Treated air emissions.

With the contaminants in a more concentrated form, they may be analyzed and subsequently designated for further treatment, recycle, or reuse before disposal. Solvent extraction has presumably improved the condition of the solids but often the solids need dewatering, treatment for residual organic compounds, additional separation, stabilization, or other treatment. The water from the dewatering process, the solids, and the water from the extractor need analysis to choose the most appropriate treatment and disposal. Typically solvent extraction units are designed to produce negligible air emissions, but significant levels of emissions may occur during waste preparation (U.S. EPA, 1990b). The units are a closed-loop design and the solvent is recycled and reused.

The primary advantage of solvent extraction is the treatability of a wide variety of media. This is in contrast to soil washing, the success of which is heavily dependent on the particle size distribution.

Some disadvantages of the process are that solvent extraction:

1) does not destroy the contaminants;
2) may not be appropriate for contaminants with high vapor pressures because these compounds may be removed with the solvent in the separation process instead of remaining with the concentrated contaminant stream;
3) is compromised by the presence of detergents and emulsifiers which compete with the solvent in dissolving the contaminants;
4) may leave residual solvent and contaminant concentrations in the treated waste;
5) is not effective for high molecular weight or hydrophilic compounds; and
6) may use flammable or mildly toxic solvents.

Figure 9-2 shows a process diagram of the solvent extraction process.

A variety of solvent extraction systems have been developed to treat several types of contamination. Six systems are described below.

CF Systems

Probably the most widely used solvent extraction system is the CF Systems which uses liquified hydrocarbons such as propane and butane as the solvent to treat soil and sludge, and carbon dioxide to treat wastewater. Water is added to the waste to enable pumping of the material through the extraction process. Particles greater than 1/8 inch in diameter are removed. In some cases, oversize particles are reduced in size for subsequent processing. The pH is adjusted in the feed to minimize corrosion of metallic components of the treatment system. CF Systems has been used at a 50 tons/day capacity to remediate refinery sludge and at 1.5 gallons/minute to treat sediments with PCBs (U.S. EPA, 1990b).

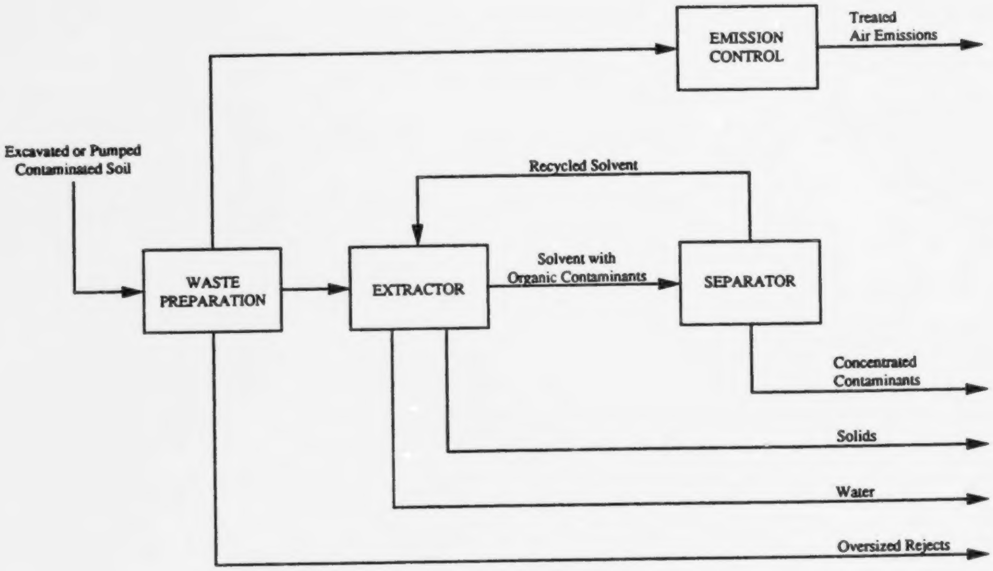
EMISSION CONTROL
Treated Air Emissions
Excavated or Pumped Contaminated Soil
Recycled Solvent
WASTE PREPARATION
EXTRACTOR
Solvent with Organic Contaminants
SEPARATOR
Concentrated Contaminants
Solids
Water
Oversized Rejects

Figure 9-2. Schematic Diagram of Solvent Extraction Process

RCC B.E.S.T.™

RCC's B.E.S.T.™ system does not need a pumpable waste and uses aliphatic amines (often triethylamine) as the solvent. Feed pH is adjusted to alkaline conditions and objects over one inch in size are removed. The process operates at near ambient temperature and pressure. Due to its high vapor pressure and low boiling point azeotrope formation, triethylamine is removed with steam stripping. The full-scale system has treated refinery waste streams at 100 tons/day and PCB-contaminated petroleum sludge at 70 tons/day. The bench-scale system has treated oil/grease contamination and sediments with PCBs in a six kilogram batch process.

ENSR

The ENSR system is currently under development and is a mobile solvent extraction unit that can process contaminated soils and sludges at a rate of five to ten cubic yards per hour. Using a proprietary solvent and reagent, the system is designed to operate without significant pretreatment or water use.

Extraksol™

The Sanivan Group in Montreal, Canada, developed the Extraksol™ process in 1984. The system has been used to treat PCBs, oil, grease, polyaromatic hydrocarbons (PAHs), and pentachlorophenol in a one ton per hour mobile unit that uses a proprietary solvent. This small unit may treat up to 300 tons of material. Sanivan is developing a full-scale unit to treat six to eight tons/hour of waste.

Harmon Environmental Services and Acurex Corporation

In a joint venture, Harmon Environmental Services and Acurex Corporation are developing a solvent soil washer/extractor system for on site remediation. The U. S. Environmental Protection Agency has sponsored bench-scale studies of treating No. 2 fuel oil.

Low Energy Extraction Process (LEEP)

The patented LEEP process treats soils, sediments, and sludges on site with common hydrophilic and hydrophobic organic solvents to remediate such pollutants as PCBs.

9.1.3 Soil Flushing

Soil flushing differs from soil washing and solvent extraction in that it is an *in situ* process in which the solvent is sprayed over the contaminated area, percolates through the soil and dissolves the contaminants. Elutriate is collected in a series of wells and drains. Flushing solutions may include the following:

1) Water for water-soluble contaminants;
2) Acidic aqueous solutions for metals and basic organic contaminants;
3) Basic aqueous solutions for some phenols, complexing and chelating agents and for metals such as zinc, tin, and lead; and
4) Surfactants.

Several factors merit consideration in the soil flushing process. Laboratory tests are essential to determine the best flushing solution for the types of soil and contaminants present. The flushing solution may affect the soil such that removal is hindered and it may also alter the soil's physical and chemical properties after remediation. Aerobic and anaerobic biodegradation may occur, also affecting the soil and contaminant composition. Solvents and contaminants may migrate into uncontaminated areas and also be resistant to removal due to soil heterogeneity (Chambers, C.D., et al., 1990). A process diagram for soil flushing is shown in Figure 9-3.

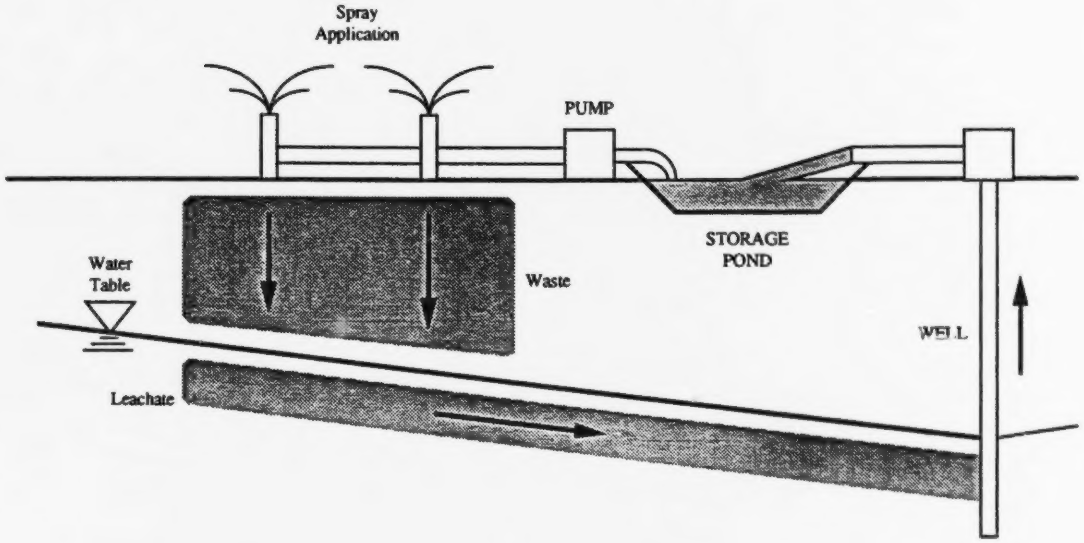
Spray Application
PUMP
Water Table
Waste
STORAGE POND
WELL
Leachate

Figure 9-3. Generalized Soil Flushing Process Flow Diagram

9.2 Identification of Air Emission Points

In the soil washing process the greatest potential for emissions of volatile contaminants occurs in the excavation, feed preparation, and extraction process. Collected emissions from these processes are typically treated by carbon adsorption or incineration (U.S. EPA, 1990a). Because soil washing occurs in liquid and solid phases, volatile compounds emitted evolve primarily due to their vapor pressures in these phases. The waste streams also have the potential to be sources of VOC emissions.

Solvent extraction may also produce emissions during excavation and soil transport and from contaminated oversize rejects (U.S. EPA, 1990b). Because the solvent recovery process involves vaporization of the solvent, fugitive emissions are possible from this as well as other stages of the solvent process, including the waste streams.

Emissions from soil flushing may emanate from the soil surface, solvent storage vessels and spray system, and from locations where the contaminant-laden flushing solution surfaces.

9.3 Typical Air Emission Species of Concern

In addition to the contaminants that may volatilize, the solvents themselves may be cause for concern. Products of aerobic and anaerobic decomposition are also possible.

9.4 Summary of Air Emissions Data

No data were identified for the air emissions from soil washing, solvent extraction, and soil flushing. Information on emissions from excavation may be found in Section 8.

9.5 Identification of Applicable Control Technologies

Carbon adsorption and incineration are typical controls used to treat collected emissions. In solvent extraction, volatile solvents are recovered and recycled. These control technologies are described in Section 5.5.

9.6 Capital and Operating Costs for Remediation

Cost for remediating contaminated soil by soil washing range from $53 to $215 per ton of feed soil, according to information from vendors of the equipment. The more expensive processes included in the cost range cover disposal of soil residue (U.S. EPA, 1990a).

Solvent extraction costs are most influenced by waste volume, number of extraction stages, operating parameters, and lost time. Operating parameters include labor, maintenance, setup, decontamination, and demobilization and lost time may result from delays in equipment operation. The choice of solvent, solvent/waste ration, feed rate, extractor residence time and number of passes through the extractor determine the efficiency of the process. Estimated costs range from $105 to $525. It is not clear whether this estimate includes emissions controls.

No cost data are available on soil flushing although costs are moderate if inexpensive flushing solutions are used and no excavation takes place.

9.7 Capital and Operating Costs for Emission Controls

The CF System Organic Extraction Process was used to remediate PCB contamination in New Bedford Harbor in Massachusetts (Valentinetti, R., 1990a and 1990b). Using liquefied propane and butane, costs were estimated to range between

$150/ton and $450/ton. These estimates do not include emissions control. General costs for controlling point source emissions are given in Section 5.7.

9.8 Equations/Models for Estimating Emissions

No equations or models for predicting the air emissions from these processes were identified.

9.9 Case Studies of Remediation and Air Emissions

Given the lack of air emissions data, no suitable case studies showing emissions were found for these processes. Remediation performance data, however, were available and Tables 9-1 through 9-3 show selected results of treatments at several sites. Further information may be obtained from the relevant documents listed int he bibliography.

9.10 References

Chambers C.D., et al. Handbook of In Situ Treatment of Hazardous Waste - Contaminated Soils. EPA/540/2-90/002 (NTIS PB90-155607). January 1990.

U.S. EPA, 1990a. Engineering Bulletin - Soil Washing Treatment. EPA/540/2-90/017 (NTIS PB91-228056). September 1990.

U.S. EPA, 1990b. Engineering Bulletin - Solvent Extraction Treatment. EPA/540/2-90/013 (NTIS PB91-228015). September 1990.

Valentinetti, R. Technology Evaluation Report: CF Systems Organics Extraction System - Volume 2, New Bedford, Massachusetts. Report No. EPA-540/5-90/002 (NTIS PB90-186503). January 1990a.

Valentinetti, R. Applications Analysis Report: CF Systems Organics Extraction System - Volume 1, New Bedford, Massachusetts. Report No. EPA-540/5-90/002 (NTIS PB90-186495). August 1990b.

Table 9-1.

Removal Efficiencies for Remediation of PCB Contamination

Test	Passes	Initial Concentration (ppm PCB)	Final Concentration (ppm PCB)	Percent Removal
2	10	350	40	89%
3	3	288	82	72%
4	6	2,575	200	92%

NOTE: CF Systems Organic Extraction System, New Bedford Harbor, Massachusetts from (Valentinetti, R., 1990a). This process used liquefied propane and butane at 240 psi and 69°F to remediate contaminated sediments.

Table 9-2.

Removal Efficiencies for Remediation of API Separator Sludge

Compound	Initial Concentration ($\mu g/g$)	Final Concentration ($\mu g/g$)	Percent Removal
Benzene	30.2	0.18	99%
Toluene	16.6	0.18	99%
Ethylbenzene	30.4	0.23	99%
Total Xylenes	13.2	0.98	93%
Anthracene	28.3	0.12	100%
Benzo(a)pyrene	1.9	0.33	83%
Bis-(2-ethylhexyl)phthalate	4.1	1.04	75%
Chrysene	6.3	0.69	89%
Naphthalene	42.2	0.66	98%
Phenanthrene	28.6	1.01	96%
Pyrene	7.7	1.08	86%

NOTE: CF Systems Organic Extraction System, Port Arthur, Texas from (U.S. EPA, 1990b). This process operated at a capacity of 50 tons per day using liquefied hydrocarbon gases as the solvent.

Table 9-3.

Summary of Performance Data on Soil Washing

Process	Contaminants	Range of Removal Efficiencies	Residual Concentrations
Soil Cleaning of America	oil and grease	50 - 83%	250 - 600 ppm
Biotrol Soil Treatment System	Pentachlorophenol	90 - 95%	<115 ppm
Biotrol Soil Treatment System	other organics	85 - 95%	<1 ppm
EPA's First Generation Pilot	oil and grease	90 - 99%	<5 - 2400 ppm
Drum Screen Washer	---	---	---
MTA Remedial Resources	volatile organics	98 - 99+%	<50 ppm
MTA Remedial Resources	semi-volatile organics	98 - 99+%	<250 ppm
MTA Remedial Resources	most fuel producs	98 - 99+%	<2200 ppm
Bodemsandering Nederland BV	aromatics	>81%	>45 ppm
Bodemsandering Nederland BV	crude oil	97%	2300 ppm
Harbauer of America	total organics	96%	159 - 201 ppm
Harbauer of America	total phenols	86 - 94%	7 - 22.5 ppm
Harbauer of America	PAH	86 - 90%	91.4 - 97.5 ppm
Harbauer of America	PCB	84 - 88%	0.5 - 1.3 ppm
Heidemij Froth Flotation	oil	>99%	20 ppm
Klockner Umweltechnik	hydrocarbons	96.3%	82.05 ppm
Klockner Umweltechnik	chlorinated hydrocarbons	>75%	<0.01 ppm
Klockner Umweltechnik	aromatics	99.8%	<0.02 ppm
Klockner Umweltechnik	PAHs	95.4%	15.48 ppm
Klockner Umweltechnik	Phenol	>99.8%	<0.01 ppm

Source: U.S. EPA, 1990a.

APPENDIX A

PROPERTIES AND COMPOSITION OF VARIOUS FUEL TYPES

Brief descriptions are given below for liquified petroleum gases, gasoline, diesel fuel, jet fuel, oil, and asphalt and bitumen.

Liquified Petroleum Gases (LPG) comprise ethane, ethylene, propane, propylene, normal butane, butylene, and isobutane and are typically produced at refineries or natural gas processing plants. Normal butane added to gasoline helps to regulate its vapor pressure and isobutane serves as an alkylation feedstock and is sold as LPG.

Gasoline is petroleum derivative with over 100 components boiling from 90°F to 420°F. Additives that improve gasoline performance can change is physical properties significantly. Adding normal butane adjusts the Reid vapor pressure (RVP) so that it varies between about 9.5 psi in the winter and 13.5 psi in the summer.[1] Butane accounts for about 75% of the vapor pressure of gasoline with pentanes making up much of the remainder. Detergent additives acting as surfactants reduce the surface tension which in turn influences subsurface migration. Hydrophilic additives such as methyl-tert-butyl ether (MTBE), methanol, and ethanol boost octane numbers and considerably increase the solubility of gasoline in water[2].

Diesel Fuel is used by trucks, railroads, stationary engines, and some automobiles. The three types of diesel most commonly used are No.1 and No.2 for automobiles and trucks; and No.4, which is heavier and used by large slow-speed vehicles[3]. This middle distillate tends to be less volatile, less mobile in soil, and less water soluble than gasolines[4].

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[1] Handbook of Energy Technology and Economics, Robert A. Meyer, ed. John Wiley and Sons, 1983, NY.

[2] David K. Kreamer and Klaus J. Stetzenback, "Development of a Standard, Pure-Compound Base Gasoline Mixture for Use as a Reference in Field and Laboratory Experiments," Spring 1990, GWMR, p. 136.

[3] Handbook of Energy Technology and Economics, Robert A. Meyers, ed. John Wiley and Sons, 1983, NY, p. 217-8.

[4] "A Guide to the Assessment and Remediation of Underground Petroleum Releases," API Publication 1628, 2nd Ed., August 1989, p.9.

Jet Fuels used by commercial and military aircraft resembles kerosene and has a similar boiling range to light diesel fuels and heating oils. Jet fuels contain no more than 20% aromatic compounds[5]. This middle distillate tends to be less volatile, less mobile in soil, and less water soluble than gasolines[6].

Oil - Heating oils No.1 and No.2 are used to heat homes and businesses and the heavier oils, Nos. 4, 5, and 6 are used by shipping and industry, and have higher viscosity and pour points[7].

Asphalt and bitumen are solid phase components of crude oil that remain virtually immobile in soil because shallow subsurface temperatures rarely rise above their melting points[8].

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[5] Handbook of Energy Technology and Economics, Robert A. Meyers, ed. John Wiley and Sons, 1983, NY, p. 217-8.

[6] "A Guide to the Assessment and Remediation of Underground Petroleum Releases," API Publication 1628, 2nd Ed., August 1989, p.9.

[7] Handbook of Energy Technology and Economics, Robert A. Meyers, ed. John Wiley and Sons, 1983, NY, p. 217-8.

[8] "A Guide to the Assessment and Remediation of Underground Petroleum Releases," API Publication 1628, 2nd Ed., August 1989, p.9.

APPENDIX B

STATE CLEANUP REQUIREMENTS FOR TOTAL PETROLEUM HYDROCARBONS IN CONTAMINATED SOIL

State	Soil Cleanup Levels (ppm Total Petroleum Hydrocarbons)
Alabama	100 if >5 ft to groundwater, 10 otherwise
Alaska	100
Arizona	100
Arkansas	case by case basis
California	10-1,000 for gasoline, 100-10,000 for diesel
Colorado	case by case basis
Connecticut	10 for gasoline, case by case otherwise
Delaware	10 for gasoline, case by case otherwise
Florida	10-500 for gasoline, 50 for diesel
Georgia	500 100 (if within 0.5 to 3 miles of well)
Hawaii	50
Idaho	100 for gasoline, 1,000 for diesel
Illinois	none for TPH, 0.025 for benzene, 16.025 for BTEX
Indiana	100
Iowa	100
Kansas	100
Kentucky	background concentration
Louisiana	case by case basis
Maine	case by case basis, generally 20-50
Maryland	case by case basis
Massachusetts	100
Michigan	background concentration
Minnesota	10 for gasoline, 1 for diesel (field PID)
Mississippi	100 (BTEX) for gasoline, 100 TPH for diesel
Missouri	100
Montana	10
Nebraska	case by case basis

State	Soil Cleanup Levels (ppm Total Petroleum Hydrocarbons)
Nevada	100
New Hampshire	10 for gasoline, 100 for diesel
New Jersey	100
New Mexico	50 (TAH) for gasoline, 100 TPH for diesel
New York	case by case basis
North Carolina	10
North Dakota	case by case basis
Ohio	background concentration
Oklahoma	50
Oregon	40-130 for gasoline, 100-1,000 for diesel
Pennsylvania	case by case basis
Rhode Island	50
South Carolina	10 (BTEX) for gasoline, 100 TPH for diesel
South Dakota	10
Tennessee	100-500 for drinking water area, otherwise 250-1,000
Texas	100
Utah	50
Vermont	20 (TAH), case by case basis
Virginia	100
West Virginia	100
Washington	100 for gasoline, 200 for diesel
Wisconsin	10
Wyoming	10 if <50 ft to groundwater, 100 if >50 ft to groundwater

BTEX = benzene, toluene, ethylbenzene, xylenes
TAH = total aromatic hydrocarbons
TPH = total petroleum hydrocarbons
PID = Photoionization detector reading

Notes:
1) Values in this table are subject to change.
2) Values were taken from several sources including: Steel Tank Institute. Tank Talk, Vol. 6, Number 1, January 1991.

APPENDIX C

EXAMPLE CALCULATIONS

CONTENTS

Page

Soil Vapor Extraction (Section 5) C-2

Evaporative Emissions from SVE System at Groveland, MA Site C-3

Emissions from In-situ Biotreatment System (Section 6) C-6

Emissions from Ex-situ Biotreatment System (Section 7) C-7

Emissions from Thermal Destruction (Section 8) C-10

SAMPLE CALCULATIONS FOR SOIL VAPOR EXTRACTION
(Section 5)

Stack Emissions from Soil Vapor Extraction

Emission Factor

$$\frac{0.05\ \text{g VOC Emitted}}{\text{g VOC Removed From Soil}}$$

Hourly Emissions

- Assumptions:

  250 kg VOC removed per 10 hr workday

- Emissions:

$$\frac{250\ \text{kg VOC}}{\text{day}} \times \frac{1\ \text{day}}{10\ \text{hr}} \times \frac{1{,}000\ \text{g}}{1\ \text{kg}} \times \frac{0.05\ \text{g VOC Emitted}}{\text{g VOC Removed}} = \frac{1{,}250\ \text{g VOC Emitted}}{\text{hr}}$$

SAMPLE CALCULATIONS FOR EVAPORATIVE EMISSIONS FROM SVE AT THE GROVELAND, MA SITE
(Section 5)

Estimated Evaporative Emissions from Semi-Closed Tank of Contaminated Water (100 ppm)

Apply Simple Mass Transfer Model (Two-Film Resistance Theory)[a]

$$Q = K_i C_i M_i$$

where: Q = evaporative emissions flux ($g/m^{2.5}$);
K_i = overall mass transfer coefficient (m/s);
C_i = concentration of contaminant (mol/m^3); and
M_i = molecular weight of contaminant (g/mol).

In turn, the overall mass transfer coefficient is given by the equation:

$$\frac{1}{K_i} = \frac{1}{K_{il}} + \frac{RT}{K_{ig} H_i}$$

where: K_{il} = liquid film mass transfer coefficient for contaminant i (m/s);
K_{ig} = gas film mass transfer coefficient for contaminant i (m/s); and
H_i = Henry's Law Constant for contaminant i ($atm\text{-}m^3/mol$).

K_{il} calculated from the correlations of Mackay and Yuen[b].

K_{il} = $1.0 \times 10^{-6} + 144 + 10^{-4}\ U^{*}\ Sc_l^{-0.5}$
U^{*} = friction velocity
= $0.01\ (6.1 \times 0.63\ U_{10})^{0.5}$
U_{10} = wind speed at 10 m above water surface
= 0 for semi-covered tank at Groveland
Sc_l = Schmidt Number for Liquid Film
= $\frac{Mwater}{\rho_w D_{iw}}$
M_w = viscosity of water
P_w = density of water
D_{iw} = diffusivity of contaminant i in water

SAMPLE CALCULATIONS FOR EVAPORATIVE EMISSIONS FROM SVE AT THE GROVELAND, MA SITE
(Section 5)
(Continued)

K_{ig} calculated from correlation of Mackay and Yuen[b].

K_{ig} = $1.0 \times 10^{-3} + 46.2 \times 10^{-3}\, U^{*}\, (Sc_g)^{-0.67}$
Sc_g = Schmidt Number for gas film
= $\dfrac{\mu_{air}}{\rho_{air}\, D_{air}}$
μ = viscosity of air
ρ = density of air
D_{air} = diffusivity of contaminant i in air

Total Evaporative Emissions:

$$E_i = QA$$

E_i = emissions from contaminated water
Q_i = emissions flux (g/m^2-sec)
A = surface area of water (m^2)

Estimated Stack Emissions:

Assume uncontrolled VOC emission rate is equal to recovery rate of VOCs:

Uncontrolled Emissions = Recovery Rate
= 5,538 g VOC/hr

SAMPLE CALCULATIONS FOR EVAPORATIVE EMISSIONS FROM SVE AT THE GROVELAND, MA SITE
(Section 5)
(Continued)

Calculate controlled VOC emission rate using control efficiency for carbon canisters:

$$\text{Controlled Emissions} = \text{Recovery Rate} * \left(1 - \frac{\text{eff}}{100}\right)$$

$$= 5{,}538 * \left(1 - \frac{99.75}{100}\right)$$

$$= 6.29 \text{ g/hr}$$

Notes:

[a] Mackay, D., and P.J. Leinonen. "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere". Environmental Science and Technology. Vol. 9, No.13. December 1975.

[b] Mackay, D., and A.T.K. Yuen. "Mass Transfer Correlations of Organic Solutes from Water" Environmental Science and Technology. Vol. 17, No. 4. April 1983.

EMISSIONS FROM IN-SITU BIOTREATMENT SYSTEMS
(Section 6)

Land Farming

Emission Factor

$$\frac{0.36 \text{ g VOC Emitted}^{2}}{\text{g VOC in Waste}}$$

Hourly Emissions

- Assumptions

Volume of Waste	1,000 m^3
VOC Concentration	100 g/m^3
Treatment Time	24 hours

- Total VOC Treated (g VOC)

$$1{,}000 \text{ m}^3 \times \frac{100 \text{ g}}{\text{m}^3} = 100{,}000 \text{ g VOC}$$

- Emissions

$$100{,}000 \text{ g VOC} \times \frac{0.36 \text{ g VOC Emitted}}{\text{g VOC in Waste}} \times \frac{1}{24 \text{ hours}} = \frac{1{,}500 \text{ g VOC Emitted}}{\text{hour}}$$

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[1] Time between impoundment turnovers.
[2] Based on 24-hour period.

EMISSIONS FROM EX-SITU BIOTREATMENT SYSTEMS
(Section 7)

Flow-Through Impoundments with Mechanical Aeration

Emission Factor

$$\frac{0.8 \text{ g VOC Emitted}}{\text{g VOC in Waste}}$$

Hourly Emissions

- Assumptions

Influent Flowrate 1 m^3/min
VOC Influent Concentration 100 g/m^3 (100 ppm)

- Total VOC Treated (g VOC/hr)

$$1 \frac{m^3}{\text{min}} \text{ x } \frac{60 \text{ min}}{\text{hr}} \text{ x } \frac{100 \text{ g}}{m^3} = \frac{6{,}000 \text{ g VOC Treated}}{\text{hr}}$$

- Emissions

$$\frac{6{,}000 \text{ g VOC Treated}}{\text{hr}} \text{ x } \frac{0.8 \text{ g VOC Emitted}}{\text{g VOC in Waste}} = \frac{4{,}800 \text{ g VOC Emitted}}{\text{hr}}$$

Quiescent Impoundments

Emission Factor

$$\frac{0.12 \text{ g VOC Emitted}}{\text{g VOC in Waste}}$$

EMISSIONS FROM EX-SITU BIOTREATMENT SYSTEMS
(Section 7)
(Continued)

Hourly Emissions

- Assumptions

Influent Flowrate	1 m^3/min
VOC Influent Concentration	100 g/m^3 (100 ppm)

- Total VOC Treated (g VOC/hr)

$$1\frac{m^3}{min} \times \frac{60\ min}{hr} \ast \frac{100\ g}{m^3} = \frac{6{,}000\ g\ VOC\ Treated}{hr}$$

- Emissions

$$6{,}000\ g\ \frac{VOC\ Treated}{hr} \times \frac{0.12\ g\ VOC\ Emitted}{g\ VOC\ in\ Waste} = \frac{720\ g\ VOC\ Emitted}{hr}$$

Disposal Impoundment

Emissions

$$\frac{0.14\ g\ VOC\ Emitted}{g\ VOC\ in\ Waste}$$

Hourly Emissions

- Assumptions

Impoundment Size	15,000 m^3
VOC Influent	100 g/m^3
[1]Disposal Time	6 months

EMISSIONS FROM EX-SITU BIOTREATMENT SYSTEMS
(Section 7)
(Continued)

- Total VOC Treated (g VOC)

$$15{,}000 \text{ m}^3 \text{ x } \frac{100 \text{ g}}{\text{m}^3} = 1{,}500{,}000 \text{ g VOC}$$

- Emissions

$$1{,}500{,}000 \text{ g VOC x } \frac{0.14 \text{ g VOC Emitted}}{\text{g VOC in Waste}} \text{ x } \frac{1}{6 \text{ months}} \text{ x } \frac{1 \text{ month}}{30 \text{ days}} \text{ x } \frac{1 \text{ day}}{24 \text{ hour}} = \frac{48.6 \text{ g VOC Emitted}}{\text{hr}}$$

EMISSIONS FROM THERMAL DESTRUCTION
(Section 8)

Air Emissions from Off-Site Rotary-Kiln Incineration (Controlled)

Emission Factors:

0.1 g VOC / kg VOC in Waste
50 g Metals / kg Metal in Waste
0.01 g HCl / g Cl in Waste
0.01 g HF / g F in Waste
0.10 g SO_2 / g S in Waste
72 mg PM / m^3 flue gas
50 ppmv CO / m^3 flue gas
100 ppmv NO_x / m^3 flue gas

Assumptions:

- Incinerator

Stack Gas Flow	986 m^3/min
Waste Fed	3,400 kg/hr
Heat Load	63 MM kJ/hr

- Waste Characterization

Cl in waste	4.0%
F in waste	1.0%
S in waste	5.0%
Metal in waste	0.1%

Estimated Control Efficiencies for Acid Gas Scrubbing

HCl	99%
HF	99%
SO_2	95%

EMISSIONS FROM THERMAL DESTRUCTION
(Section 8)
(Continued)

Hourly Emissions:

VOC: $\frac{3{,}400\text{ kg}}{\text{hr}} \times \frac{0.999\text{ g Organic}}{\text{g waste}} \times \frac{0.1\text{ g VOC}}{\text{kg waste}} = 340\text{ g VOC/hr}$

Metals: $\frac{3{,}400\text{ kg}}{\text{hr}} \times \frac{0.001\text{ kg M}}{\text{kg Waste}} \times \frac{50\text{ g emitted M}}{1\text{ kg M in waste}} = 170\text{ g Metal/hr}$

HCl: $\frac{3{,}400\text{ kg waste}}{\text{hr}} \times \frac{0.04\text{ kgCl}}{\text{kg waste}} \times \frac{0.011\text{ g HF}}{\text{g F}} = 0.4\text{ g HF/hr}$

HF: $\frac{3{,}400\text{ kg waste}}{\text{hr}} \times \frac{0.01\text{ kg F}}{\text{kg waste}} \times \frac{0.11\text{ g HF}}{\text{g F}} = 0.4\text{ g HF/hr}$

SO_2: $\frac{3{,}400\text{ kg waste}}{\text{hr}} \times \frac{0.05\text{ kg S}}{\text{kg waste}} \times \frac{0.10\text{ g } SO_2}{\text{g S}} = 17.0\text{ g } SO_2\text{/hr}$

PM: $\frac{72\text{ mg PM}}{m^3} \times \frac{986\text{ m}^3}{\text{min}} \times \frac{60\text{ min}}{\text{hr}} \times \frac{\text{g}}{1{,}000\text{ mg}} = 4{,}260\text{ g PM/hr}$

NO_x: $\frac{986\text{ m}^3}{\text{min}} \times \frac{\text{gmole}}{0.0236\text{ m}^3} \times \frac{100\text{ gmole } NO_x}{10^6\text{ gmole Air}} \times \frac{60\text{ min}}{\text{hr}} \times \frac{46\text{ g}}{\text{gmole}} = 11{,}530\text{ g } NO_x\text{/hr}$

APPENDIX D

United States
Environmental Protection
Agency

Office of Emergency and
Remedial Response
Washington, DC 20460

Office of
Research and Development
Cincinnati, OH 45268

Superfund

EPA/540/2-91/008

May 1991

EPA

Engineering Bulletin
Thermal Desorption Treatment

Purpose

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants and contaminants as a principal element." The Engineering Bulletins are a series of documents that summarize the latest information available on selected treatment and site remediation technologies and related issues. They provide summaries of and references for the latest information to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their Superfund or other hazardous waste site. Those documents that describe individual treatment technologies focus on remedial investigation scoping needs. Addenda will be issued periodically to update the original bulletins.

Abstract

Thermal desorption is an ex situ means to physically separate volatile and some semivolatile contaminants from soil, sediments, sludges, and filter cakes. For wastes containing up to 10% organics or less, thermal desorption can be used alone for site remediation. It also may find applications in conjunction with other technologies or be appropriate to specific operable units at a site.

Site-specific treatability studies may be necessary to document the applicability and performance of a thermal desorption system. The EPA contact indicated at the end of this bulletin can assist in the definition of other contacts and sources of information necessary for such treatability studies.

Thermal desorption is applicable to organic wastes and generally is not used for treating metals and other inorganics. Depending on the specific thermal desorption vendor selected, the technology heats contaminated media between 200-1000°F, driving off water and volatile contaminants. Offgases may be burned in an afterburner, condensed to reduce the volume to be disposed, or captured by carbon adsorption beds.

Commercial-scale units exist and are in operation. Thermal desorption has been selected at approximately fourteen Superfund sites [1]* [2]. Three Superfund Innovative Technology Evaluation demonstrations are planned for the next year.

The final determination of the lowest cost alternative will be more site-specific than process equipment dominated. This bulletin provides information on the technology applicability, limitations, the types of residuals produced, the latest performance data, site requirements, the status of the technology, and sources for further information.

Technology Applicability

Thermal desorption has been proven effective in treating contaminated soils, sludges, and various filter cakes. Chemical contaminants for which bench-scale through full-scale treatment data exist include primarily volatile organic compounds (VOCs), semivolatiles, and even higher boiling point compounds, such as polychlorinated biphenyls (PCBs) [3][4][5][6]. The technology is not effective in separating inorganics from the contaminated medium. Volatile metals, however, may be removed by higher temperature thermal desorption systems.

Some metals may be volatilized by the thermal desorption process as the contaminated medium is heated. The presence of chlorine in the waste can also significantly affect the volatilization of some metals, such as lead. Normally the temperature of the medium achieved by the process does not oxidize the metals present in the contaminated medium [7, p. 85].

The process is applicable for the separation of organics from refinery wastes, coal tar wastes, wood-treating wastes, creosote-contaminated soils, hydrocarbon-contaminated soils, mixed (radioactive and hazardous) wastes, synthetic rubber processing wastes, and paint wastes [8, p. 2][4][9].

Performance data presented in this bulletin should not be considered directly applicable to other Superfund sites. A number of variables, such as the specific mix and distribution

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* [reference number, page number]

Table 1
RCRA Codes for Wastes Treated by Thermal Desorption

Wood Treating Wastes	K001
Dissolved Air Flotation (DAF) Float	K048
Slop Oil Emulsion Solids	K049
Heat Exchanger Bundles Cleaning Sludge	K050
American Petroleum Institute (API) Separator Sludge	K051
Tank Bottoms (leaded)	K052

Table 2
Effectiveness of Thermal Desorption on General Contaminant Groups for Soil, Sludge, Sediments, and Filter Cakes

		Effectiveness			
	Contaminant Groups	*Soil*	*Sludge*	*Sediments*	*Filter Cakes*
Organic	Halogenated volatiles	■	▼	▼	■
	Halogenated semivolatiles	■	▼	▼	■
	Nonhalogenated volatiles	■	▼	▼	■
	Nonhalogenated semivolatiles	■	▼	▼	■
	PCBs	■	▼	▼	▼
	Pesticides	■	▼	▼	▼
	Dioxins/Furans	■	▼	▼	▼
	Organic cyanides	▼	▼	▼	▼
	Organic corrosives	☐	☐	☐	☐
Inorganic	Volatile metals	■	▼	▼	▼
	Nonvolatile metals	☐	☐	☐	☐
	Asbestos	☐	☐	☐	☐
	Radioactive materials	☐	☐	☐	☐
	Inorganic corrosives	☐	☐	☐	☐
	Inorganic cyanides	☐	☐	☐	☐
Reactive	Oxidizers	☐	☐	☐	☐
	Reducers	☐	☐	☐	☐

■ Demonstrated Effectiveness: Successful treatability test at some scale completed

▼ Potential Effectiveness: Expert opinion that technology will work

☐ No Expected Effectiveness: Expert opinion that technology will not work

of contaminants, affect system performance. A thorough characterization of the site and a well-designed and conducted treatability study are highly recommended.

Table 1 lists the codes for the specific Resource Conservation and Recovery Act (RCRA) wastes that have been treated by this technology [8, p. 2][4][9]. The indicated codes were derived from vendor data where the objective was to determine thermal desorption effectiveness for these specific industrial wastes. The effectiveness of thermal desorption on general contaminant groups for various matrices is shown in Table 2. Examples of constituents within contaminant groups are provided in "Technology Screening Guide For Treatment of CERCLA Soils and Sludges" [7, p. 10]. This table is based on the current available information or professional judgment where no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show the technology was effective for that particular contaminant and medium. The ratings of potential effectiveness or no expected effectiveness are both based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular medium. When the technology is not applicable or will probably not work for a particular combination of contaminant group and medium, a no expected effectiveness rating is given. Another source of general observations and average removal efficiencies for different treatability groups is contained in the Superfund Land Disposal Restrictions (LDR) Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS, September 1990) [10] and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-06BFS, September 1990) [11].

Limitations

The primary technical factor affecting thermal desorption performance is the maximum bed temperature achieved. Since the basis of the process is physical removal from the medium by volatilization, bed temperature directly determines which organics will be removed.

The contaminated medium must contain at least 20 percent solids to facilitate placement of the waste material into the desorption equipment [3, p. 9]. Some systems specify a minimum of 30 percent solids [12, p. 6].

As the medium is heated and passes through the kiln or desorber, energy is lost in heating moisture contained in the contaminated soil. A very high moisture content can result in low contaminant volatilization or a need to recycle the soil through the desorber. High moisture content, therefore, causes increased treatment costs.

Material handling of soils that are tightly aggregated or largely clay, or that contain rock fragments or particles greater than 1-1.5 inches can result in poor processing performance due to caking. Also, if a high fraction of fine silt or clay exists in the matrix, fugitive dusts will be generated [7, p. 83] and a greater dust loading will be placed on the downstream air pollution control equipment [12, p. 6].

The treated medium will typically contain less than 1 percent moisture. Dust can easily form in the transfer of the treated medium from the desorption unit, but can be mitigated by water sprays. Normally, clean water from air pollution control devices can be used for this purpose.

Although volatile organics are the primary target of the thermal desorption technology, the total organic loading is limited by some systems to up to 10 percent or less [13, p. II-

30]. As in most systems that use a reactor or other equipment to process wastes, a medium exhibiting a very high pH (greater than 11) or very low pH (less than 5) may corrode the system components [7, p. 85].

There is evidence with some system configurations that polymers may foul and/or plug heat transfer surfaces [3, p. 9]. Laboratory/field tests of thermal desorption systems have documented the deposition of insoluble brown tars (presumably phenolic tars) on internal system components [14, p. 76].

High concentrations of inorganic constituents and/or metals will likely not be effectively treated by thermal desorption. The maximum bed temperature and the presence of chlorine can result in volatilization of some inorganic constituents in the waste, however.

Technology Description

Thermal desorption is any of a number of processes that use either indirect or direct heat exchange to vaporize organic contaminants from soil or sludge. Air, combustion gas, or inert gas is used as the transfer medium for the vaporized components. Thermal desorption systems are physical separation processes and are not designed to provide high levels of organic destruction, although the higher temperatures of some systems will result in localized oxidation and/or pyrolysis. Thermal desorption is not incineration, since the destruction of organic contaminants is not the desired result. The bed temperatures achieved and residence times designed into thermal desorption systems will volatilize selected contaminants, but typically not oxidize or destroy them. System performance is typically measured by comparison of untreated soil/sludge contaminant levels with those of the processed soil/sludge. Soil/sludge is typically heated to 200 - 1000° F, based on the thermal desorption system selected.

Figure 1 is a general schematic of the thermal desorption process.

Waste material handling (1) requires excavation of the contaminated soil or sludge or delivery of filter cake to the system. Typically, large objects greater than 1.5 inches are screened from the medium and rejected. The medium is then delivered by gravity to the desorber inlet or conveyed by augers to a feed hopper [8, p. 1].

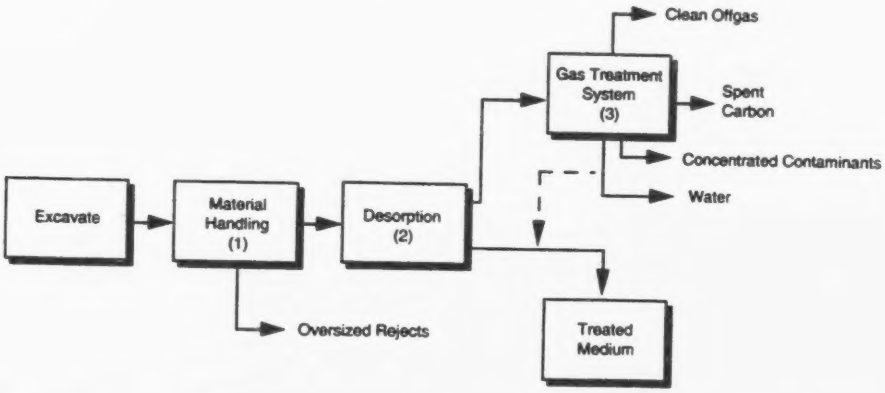
Significant system variation exists in the desorption step (2). The dryer can be an indirectly fired rotary asphalt kiln, a single (or set of) internally heated screw auger(s), or a series of externally heated distillation chambers. The latter process uses annular augers to move the medium from one volatilization zone to the next. Additionally, testing and demonstration data exist for a fluidized-bed desorption system [12].

The waste is intimately contacted with a heat transfer surface, and highly volatile components (including water) are driven off. An inert gas, such as nitrogen, may be injected in a countercurrent sweep stream to prevent contaminant combustion and to vaporize and remove the contaminants [8, p. 1][4]. Other systems simply direct the hot gas stream from the desorption unit [3, p. 5][5].

The actual bed temperature and residence time are the primary factors affecting performance in thermal desorption. These parameters are controlled in the desorption unit by using a series of increasing temperature zones [8, p. 1], multiple passes of the medium through the desorber where the operating temperature is sequentially increased, separate compartments where the heat transfer fluid temperature is higher, or sequential processing into higher temperature zones [15][16]. Heat transfer fluids used to date include hot combustion gases, hot oil, steam, and molten salts.

Offgas from desorption is typically processed (3) to remove particulates. Volatiles in the offgas may be burned in an afterburner, collected on activated carbon, or recovered in condensation equipment. The selection of the gas treatment system will depend on the concentrations of the contaminants, cleanup standards, and the economics of the offgas treatment system(s) employed.

Figure 1
Schematic Diagram of Thermal Desorption



Process Residuals

Operation of thermal desorption systems typically creates up to six process residual streams: treated medium, oversized medium rejects, condensed contaminants and water, particulate control system dust, clean offgas, and spent carbon (if used). Treated medium, debris, and oversized rejects may be suitable for return onsite.

Condensed water may be used as a dust suppressant for the treated medium. Scrubber purge water can be purified and returned to the site wastewater treatment facility (if available), disposed to the sewer [3, p. 8] [8, p. 2] [4, p. 2], or used for rehumidification and cooling of the hot, dusty media. Concentrated, condensed organic contaminants are containerized for further treatment or recovery.

Dust collected from particulate control devices may be combined with the treated medium or, depending on analyses for carryover contamination, recycled through the desorption unit.

Clean offgas is released to the atmosphere. If used, spent carbon may be recycled by the original supplier or other such processor.

Site Requirements

Thermal desorption systems are transported typically on specifically adapted flatbed semitrailers. Since most systems consist of three components (desorber, particulate control, and gas treatment), space requirements on site are typically less than 50 feet by 150 feet, exclusive of materials handling and decontamination areas.

Standard 440V, three-phase electrical service is needed. Water must be available at the site. The quantity of water needed is vendor and site specific.

Treatment of contaminated soils or other waste materials require that a site safety plan be developed to provide for personnel protection and special handling measures. Storage should be provided to hold the process product streams until they have been tested to determine their acceptability for disposal or release. Depending upon the site, a method to store waste that has been prepared for treatment may be necessary. Storage capacity will depend on waste volume.

Onsite analytical equipment capable of determining site-specific organic compounds for performance assessment make the operation more efficient and provide better information for process control.

Performance Data

Several thermal desorption vendors report performance data for their respective systems ranging from laboratory treatability studies to full-scale operation at designated Superfund sites [17][9][18]. The quality of this information has not been determined. These data are included as a general guideline to the performance of thermal desorption equipment, and may not be directly transferrable to a specific Superfund site. Good site characterization and treatability studies are essential in further refining and screening the thermal desorption technology.

Chem Waste Management's (CWM's) X*TRAX™ System has been tested at laboratory and pilot scale. Pilot tests were performed at CWM's Kettleman Hills facility in California. Twenty tons of PCB- and organic-contaminated soils were processed through the 5 TPD pilot system. Tables 3 and 4 present the results of PCB separation from soil and total hydrocarbon emissions from the system, respectively [4].

During a non-Superfund project for the Department of Defense, thermal desorption was used in a full-scale demonstration at the Tinker Air Force Base in Oklahoma. The success of this project led to the patenting of the process by Weston Services, Inc. Since then, Weston has applied its low-temperature thermal treatment (LT^3) system to various contaminated soils at bench-scale through full-scale projects [19]. Table 5 presents a synopsis of system and performance data for a full-scale treatment of soil contaminated with No. 2 fuel oil and gasoline at a site in Illinois.

Canonie Environmental has extensive performance data for its Low Temperature Thermal Aeration (LTTA℠) system at full-scale operation (15-20 cu. yds. per hour). The LTTA℠ has been applied at the McKin (Maine), Ottati and Goss (New Hampshire) and Cannon Engineering Corp. (Massachusetts) Superfund sites. Additionally, the LTTA℠ has been used at the privately-funded site in South Kearney (New Jersey). Table

Table 3
PCB Contaminated Soils
Pilot X*TRAX™ [4]

Matrix	*Feed (ppm)*	*Product (ppm)*	*Removal (%)*
Clay	5,000	24	99.3
Silty Clay	2,800	19	99.5
Clay	1,600	4.8	99.7
Sandy	1,480	8.7	99.1
Clay	630	17	97.3

Table 4
Pilot X*TRAX™
TSCA Testing - Vent Emissions [4]

Total Hydrocarbons (ppm-V)				
Before Carbon	*After Carbon*	*Removal (%)*	*VOC (lbs/day)*	*PCB* (mg/m³)*
1,320	57	95.6	0.02	<0.00056
1,031	72	93.0	0.03	<0.00055
530	35	93.3	0.01	<0.00051
2,950	170	94.2	0.07	<0.00058
2,100	180	91.4	0.08	<0.00052

*Note: OSHA permits 0.50 mg/m^3 PCB (1254) for 8-hr exposure.

6 presents a summary of Canonie LTTA^{SM} data [5]. The Cannon Engineering (Mass) site, which was not included in Table 6, successfully treated a total of 11,330 tons of soil, containing approximately 1803 lbs. of VOC [20].

T.D.I. Services, Inc. has demonstrated its HT-5 Thermal Distillation Process at pilot- and full-scale for a variety of RCRA-listed and other wastes that were prepared to simulate American Petroleum Institute (API) refinery sludge [8]. The company has conducted pilot- and full-scale testing with the API sludge to demonstrate the system's ability to meet Land Ban Disposal requirements for K048 through K052 wastes. Independent evaluation by Law Environmental confirms that the requirements were met, except for TCLP levels of nickel, which were blamed on a need to "wear-in" the HT-5 system [21, p. ii].

Remediation Technologies, Inc. (ReTec) has performed numerous tests on RCRA-listed petroleum refinery wastes. Table 7 presents results from treatment of refinery vacuum

Table 5
Full-Scale Performance Results for the LT^3 System [19]

Contaminant	*Soil Range (ppb)*	*Treated Range (ppb)*	*Range of Removal Efficiency*
Benzene	1000	5.2	99.5
Toluene	24000	5.2	99.9
Xylene	110000	<1.0	>99.9
Ethyl benzene	20000	4.8	99.9
Napthalene	4900	<330	>99.3
Carcinogenic			
Priority PNAs	<6000	<330–590	<90.2–94.5
Non-carcinogenic			
Priority PNAs	890–6000	<330–450	<62.9–94.5

Table 6
Summary Results of the LTTA^{SM} Full-Scale Cleanup Tests [5]

Site	*Processed*	*Contaminant*	*Soil (ppm)*	*Treated (ppm)*
S. Kearney	16000 tons	VOCs PAHs	177.0 (avg.) 35.31 (avg.)	0.87 (avg.) 10.1 (avg.)
McKin	>9500 cu yds 2000 cu yds	VOCs PAHs	ND-3310	ND-0.04 <10
Ottati & Goss	4500 cu yds	VOCs	1500 (avg.)	<0.2 (avg.)

Table 7
ReTec Treatment Results-Refinery Vacuum Filter Cake (A) [3]

Compound	*Original Sample (ppm)*	*Treated Sample (ppm)*	*Removal Efficiency (%)*
Naphthalene	<0.1	<0.1	---
Acenaphthylene	<0.1	<0.1	---
Acenaphthene	<0.1	<0.1	---
Fluorene	10.49	<0.1	>98.9
Phenanthrene	46.50	<0.1	>99.3
Anthracene	9.80	<0.1	>96.6
Fluoranthrene	73.94	<0.1	>99.8
Pyrene	158.37	<0.1	>99.9
Benzo(b)anthracene	56.33	1.43	97.5
Chrysene	64.71	<0.1	>99.9
Benzo(b)fluoranthene	105.06	2.17	97.9
Benzo(k)fluoranthene	225.37	3.64	98.4
Benzo(a)pyrene	174.58	1.89	98.9
Dibenz(ab)antracene	477.44	10.25	97.8
Benzo(ghi)perylene	163.53	5.09	96.6
Indeno(123-cd)pyrene	122.27	4.16	96.6
Treatment Temperature: 450°F			

Table 8
ReTec Treatment Results-Creosote Contaminated Clay [3]

Compound	*Original Sample (ppm)*	*Treated Sample (ppm)*	*Removal Efficiency (%)*
Naphthalene	1321	<0.1	>99.9
Acenaphthylene	<0.1	<0.1	---
Acenaphthene	293	<0.1	>99.96
Fluorene	297	<0.1	>99.96
Phenanthrene	409	1.6	99.6
Anthracene	113	<0.1	>99.7
Fluoranthrene	553	1.5	99.7
Pyrene	495	2.0	99.6
Benzo(b)anthracene	59	<0.1	>99.99
Chrysene	46	<0.1	>99.8
Benzo(b)fluoranthene	14	2.5	82.3
Benzo(k)fluoranthene	14	<0.1	>99.8
Benzo(a)pyrene	15	<0.1	>99.9
Dibenzo(ab)anthracene	<0.1	<0.1	---
Benzo(ghi)perylene	7	<0.1	>99.4
Indeno(123-cd)pyrene	3	<0.1	>99.3
Treatment Temperature: 500°F			

Table 9
ReTec Treatment Results-Coal Tar Contaminated Soils [3]

Compound	Original Sample (ppm)	Treated Sample (ppm)	Removal Efficiency (%)
Benzene	1.7	<0.1	>94
Toluene	2.3	<0.1	>95
Ethylbenzene	1.6	<0.1	>93
Xylenes	6.3	<0.3	>95
Naphthalene	367	<1.7	>99
Fluorene	114	<0.2	>99
Phenanthrene	223	18	91.9
Anthracene	112	7.0	93.8
Fluoranthrene	214	15	93.0
Pyrene	110	11	90.0
Benzo(b)anthracene	56	<1.4	>97
Chrysene	58	3.7	93.6
Benzo(b)fluoranthene	45	<1.4	>97
Benzo(k)fluoranthene	35	<2.1	>94
Benzo(a)pyrene	47	<0.9	>98
Benzo(ghi)perylene	24	<1.1	>95
Indeno(123-cd)pyrene	27	<6.2	>77
Treatment Temperature: 450°F			

filter cake. Tests with creosote-contaminated clay and coal tar-contaminated soils showed significant removal efficiencies (Tables 8 and 9). All data were obtained through use of ReTec's 100 lb/h pilot scale unit processing actual industrial process wastes [3].

Recycling Sciences International, Inc. (formerly American Toxic Disposal, Inc.) has tested its Desorption and Vaporization Extraction System (DAVES), formerly called the Vaporization Extraction System (VES), at Waukegan Harbor, Illinois. The pilot-scale test demonstrated PCB removal from material containing up to 250 parts per million (ppm) to levels less than 2 ppm [12].

RCRA LDRs that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements for CERCLA response actions. Thermal desorption can produce a treated waste that meets treatment levels set by BDAT but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where thermal desorption does not meet these levels, it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. Treatability variances are justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS, September 1990) [10], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-06BFS, September 1990) [11]. Another approach could be to use other treatment techniques in series with thermal desorption to obtain desired treatment levels.

Technology Status

Significant theoretical research is ongoing [22][23], as well as direct demonstration of thermal desorption through both treatability testing and full-scale cleanups.

A successful pilot-scale demonstration of Japanese soils "roasting" was conducted in 1980 for the recovery of mercury from highly contaminated (up to 15.6 percent) soils at a plant site in Tokyo. The high concentration of mercury made recovery and refinement to commercial grade (less than 99.99 percent purity) economically feasible [24].

In this country, thermal desorption technologies are the selected remedies for one or more operable units at fourteen Superfund sites. Table 10 lists each site's location, primary contaminants, and present status [1][2].

Most of the hardware components of thermal desorption are available off the shelf and represent no significant problem of availability. The engineering and configuration of the systems are similarly refined, such that once a system is designed full-scale, little or no prototyping or redesign is required.

On-line availability of the full-scale systems described in this bulletin is not documented. However, since the ex situ system can be operated in batch mode, it is expected that component failure can be identified and spare components fitted quickly for minimal downtime.

Several vendors have documented processing costs per ton of feed processed. The overall range varies from $80 to $350 per ton processed [6][4, p. 12][5][3, p. 9]. Caution is recommended in using costs out of context because the base year of the estimates vary. Costs also are highly variable due to the quantity of waste to be processed, term of the remediation contract, moisture content, organic constituency of the contaminated medium, and cleanup standards to be achieved. Similarly, cost estimates should include such items as preparation of Work Plans, permitting, excavation, processing itself, QA/QC verification of treatment performance, and reporting of data.

EPA Contact

Technology-specific questions regarding thermal desorption may be directed to:

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Table 10
Superfund Sites Specifying Thermal Desorption as the Remedial Action

Site	*Location*	*Primary Contaminants*	*Status*
Cannon Engineering (Bridgewater Site)	Bridgewater, MA (1)	VOCs (Benzene, TCE & Vinyl Chloride)	Project completed 10/90
McKin	McKin, ME (1)	VOCs (TCE, BTX)	Project completed 2/87
Ottati & Goss	New Hampshire (1)	VOCs (TCE; PCE; 1, 2-DCA, and Benzene)	Project completed 9/89
Wide Beach	Brandt, NY (2)	PCBs	In design • pilot study available 5/91
Metaltec/Aerosystems	Franklin Borough, NJ (2)	TCE and VOCs	In design • remedial design complete • remediation starting Fall '91
Caldwell Trucking	Fairfield, NJ (2)	VOCs (TCE, PCE, and TCA)	In design
Outboard Marine/ Waukegan Harbor	Waukegan Harbor, IL (5)	PCBs	In design • treatability studies complete
Reich Farms	Dover Township, NJ (02)	VOCs and Semivolatiles	Pre-design
Re-Solve	North Dartmouth, MA (1)	PCBs	In design • pilot study June/July '91
Waldick Aerospace Devices	New Jersey (2)	TCE and PCE	In design
Wamchem	Burton, SC (4)	BTX and SVOCs (Naphthalene)	In design • pilot study available 5/91
Fulton Terminals	Fulton, NY (2)	VOCs (Xylene, Styrene, TCE, Ethylbenzene, Toluene) and some PAHs	Pre-design
Stauffer Chemical	Cold Creek, AL (4)	VOCs and pesticides	Pre-design
Stauffer Chemical	Le Moyne, AL (4)	VOCs and pesticides	Pre-design

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APPENDIX E - ARTICLE ON SOIL VAPOR EXTRACTION

(Source: Pedersen, T.A., and J.T. Curtis. Handbook on Soil Vapor Extraction Technology. EPA/540/2-91-003. February 1991.

A PRACTICAL APPROACH TO THE DESIGN, OPERATION, AND MONITORING OF IN-SITU SOIL VENTING SYSTEMS

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INTRODUCTION

When operated properly, in-situ soil venting or vapor extraction can be one of the more cost-effective remediation processes for soils contaminated with gasoline, solvents, or other relatively volatile compounds. A "basic" system, such as that shown in Figure E-1, couples vapor extraction (recovery) wells with blowers or vacuum pumps to remove vapors from the vadose zone and thereby reduce residual levels of soil contaminants. More complex systems incorporate trenches, air injection wells, passive wells, and surface seals. Above-ground treatment systems condense, adsorb, or incinerate vapors; in some cases vapors are simply emitted to the atmosphere through diffuser stacks. In-situ soil venting is an especially attractive treatment option because the soil is treated in place, sophisticated equipment is not required, and the cost is typically lower than other options.

The basic phenomena governing the performance of soil venting systems are easily understood. By applying a vacuum and removing vapors from extraction wells, vapor flow through the unsaturated soil zone is induced. Contaminants volatilize from the soil matrix and are swept by the carrier gas flow (primarily air) to the extraction wells or trenches. Many complex processes occur on the microscale, however, the three main factors that control the performance of a venting operation are the chemical composition of the contaminant, vapor flowrates through the unsaturated zone, and the flowpath of carrier vapors relative to the location of the contaminants.

The components of soil venting systems are typically off-the-shelf items, and the installation of wells and trenches can be done by most reputable environmental firms. However, the design, operation, and monitoring of soil venting systems is not trivial. In fact, choosing whether or not

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[a]Shell Development/[b]Shell Oil Company, Westhollow Research Center
Houston, TX 77152-1380

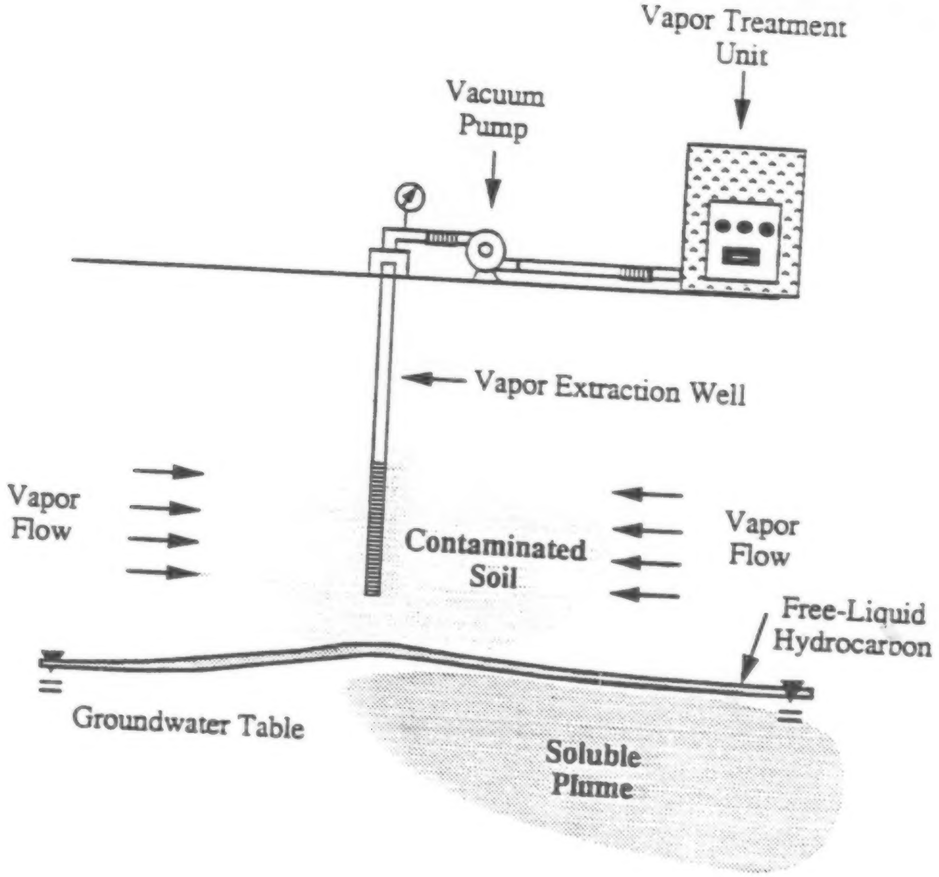
Vapor Treatment Unit
Vacuum Pump
Vapor Extraction Well
Vapor Flow
Contaminated Soil
Vapor Flow
Free-Liquid Hydrocarbon
Groundwater Table
Soluble Plume

Figure E-1. "Basic" In-Situ Soil Venting System venting should be applied at a given site is a difficult question in itself. If one decides to utilize venting, design questions involving the number of wells, well spacing, well location, well construction, and vapor treatment systems must then be answered. It is the current state-of-the-art that such questions are answered more by instinct than by rigorous logic. This is evidenced by the published soil venting "success stories" (see Hutzler et al.[1] for a good review), which rarely include insight into the design process.

In this paper we suggest a series of steps and questions that must be followed and answered in order to a) decide if venting is appropriate at a given site, and b) to design cost-effective in-situ soil venting systems. This series of steps and questions forms a "decision tree" process that could be easily incorporated in a PC-based expert system. In the development of this approach we will attempt to identify the limitations of in-situ soil venting, and subjects or behavior that are difficult to quantify and for which future study is needed.

THE "PRACTICAL APPROACH"

Figure E-2 presents a flowchart of the process discussed in this paper. Each step of the flowchart is discussed below in detail, and where appropriate, examples are given.

The Site Investigation

Whenever a soil contamination problem is detected or suspected, a site investigation is conducted to characterize and delineate the zone of soil and groundwater contamination. Often the sequence of steps after initial response and abatement is as follows:

(a) *background review*: Involves assembling historical records, plot plans, engineering drawings (showing utility lines), and interviewing site personnel. This information is used to help identify the contaminant, probable source of release, zone of contamination, and potentially impacted areas (neighbors, drinking water supplies, etc.).

(b) *preliminary site screening*: Preliminary screening tools such as soil-gas surveys and cone penetrometers are used to roughly define the zone of contamination and the site geology. Knowledge of site geology is essential to determine probable migration of contaminants through the unsaturated zone.

(c) *detailed site characterization*: Soil borings are drilled and monitoring wells are installed based on the results from steps (a) and (b).

(d) *contaminant characterization*: soil and groundwater samples are analyzed to determine contaminant concentrations and compositions.

Costs associated with site investigations can be relatively high depending on the complexity of the site and size of the spill or leak. For large spills and complex site geological/hydrogeological conditions, site

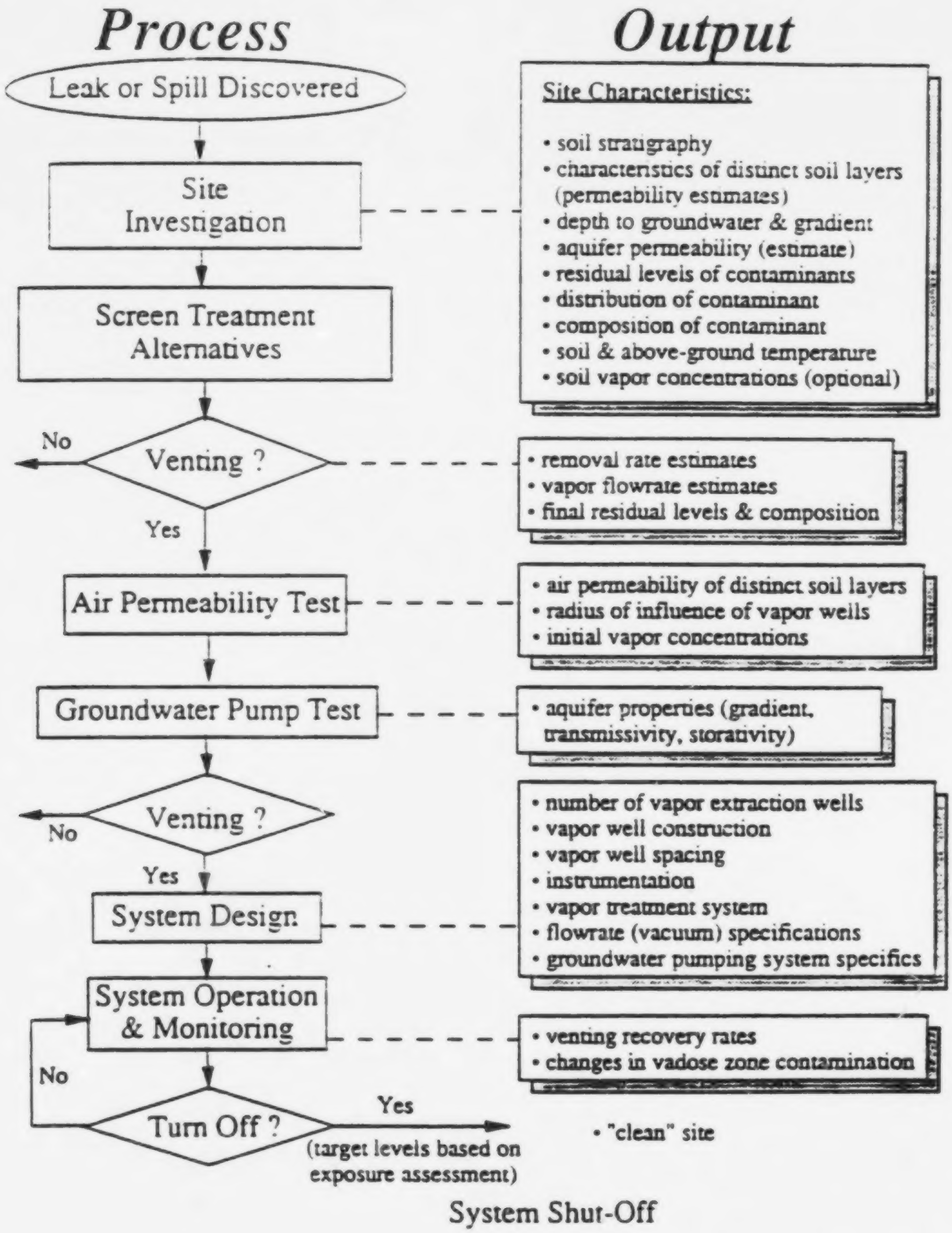
Process
Output
Leak or Spill Discovered
Site Investigation
Screen Treatment Alternatives
Venting ?
No
Yes
Air Permeability Test
Groundwater Pump Test
Venting ?
No
Yes
System Design
System Operation & Monitoring
No
Turn Off ?
Yes
(target levels based on exposure assessment)
System Shut-Off
Site Characteristics:
• soil stratigraphy
• characteristics of distinct soil layers (permeability estimates)
• depth to groundwater & gradient
• aquifer permeability (estimate)
• residual levels of contaminants
• distribution of contaminant
• composition of contaminant
• soil & above-ground temperature
• soil vapor concentrations (optional)
• removal rate estimates
• vapor flowrate estimates
• final residual levels & composition
• air permeability of distinct soil layers
• radius of influence of vapor wells
• initial vapor concentrations
• aquifer properties (gradient, transmissivity, storativity)
• number of vapor extraction wells
• vapor well construction
• vapor well spacing
• instrumentation
• vapor treatment system
• flowrate (vacuum) specifications
• groundwater pumping system specifics
• venting recovery rates
• changes in vadose zone contamination
• "clean" site

Figure E-2. In-Situ Soil Venting System Design Process.

investigation costs are often comparable to remediation costs. In addition, the choice and design of a remediation system is based on the data obtained during the site investigation. For these reasons it is important to insure that specific information is collected, and to validate the quality of the data.

If it is presumed that in-situ soil venting will be a candidate for treatment, then the following information needs to be obtained during the preliminary site investigation:

(a) *site geology* - this includes soil type and subsurface stratigraphy. While they are not essential, the moisture content, total organic carbon, and permeability of each distinct soil layer also provides useful information that can be used to choose and design a remediation system.

(b) *site hydrogeology* - the water table depth and gradient must be known, as well as estimates of the aquifer permeability.

(c) *contaminant composition, distribution and residual levels* - soil samples should be analyzed to determine which contaminants are present at what levels. Recommended analytical methods should be used to identify target compounds (i.e., benzene, toluene, or xylenes) and total hydrocarbons present. For soil analyses these methods are:

EPA 8240 - volatile organic chemicals
EPA 8270 - semi-volatile organic chemicals
EPA 418.1 - total petroleum hydrocarbons

The corresponding water analyses methods are:

EPA 624 - volatile organic chemicals
EPA 625 - semi-volatile organic chemicals
EPA 418.1 - total petroleum hydrocarbons

With the current high cost of chemical analyses it is important to intelligently select which analyses should be performed and which samples should be sent to a certified laboratory. Local regulations usually require that a minimum number of soil borings be performed, and target compounds must be analyzed for based on the suspected composition of the contamination. Costs can be minimized and more data obtained by utilizing field screening tools, such as hand-held vapor meters or portable field GC's. These instruments can be used to measure both residual soil contamination levels and headspace vapors above contaminated soils. At a minimum, soil samples corresponding to lithology changes or obvious changes in residual levels (based on visual observations or odor) should be analyzed.

For complex contamination mixtures, such as gasoline, diesel fuel, and solvent mixtures, it is not practical or necessary to identify and quantify each compound present. In such cases it is recommended that a "boiling point" distribution be measured for a representative sample of the residual contamination. Boiling point distribution curves, such as shown in Figure E-3 for "fresh" and "weathered" gasoline samples, can be constructed from GC analyses of the soil residual contamination (or free-product) and knowledge of the GC elution behavior of a known series of compounds (such as straight-chain alkanes). Compounds generally elute from a GC packed column in the order of increasing boiling point, so a boiling point distribution curve is constructed by grouping all unknowns that elute between two known peaks (i.e. between n-hexane and n-heptane). Then they are assigned an average boiling point, molecular weight, and vapor pressure. Use of this data will be explained below.

(d) *temperature* - both above- and below-ground surface.

The cone penetrometer, which is essentially an instrumented steel rod that is driven into the soil, is becoming a popular tool for preliminary site screening investigations. By measuring the shear and normal forces on the leading end of the rod, soil structure, and hence permeability can be defined. Some cone penetrometers are also constructed to allow the collection of vapor or groundwater samples. This tool has several advantages over conventional soil boring techniques (as a preliminary site characterization tool): the subsurface soil structure can be defined better, no soil cuttings are generated, and more analyses can be performed per day.

Results from the preliminary site investigation should be summarized in contour plots, fence diagrams, and tables prior to analyses.

Deciding if Venting is Appropriate

As stated above, the three main factors governing the behavior of any in-situ soil venting operation are the vapor flow rate, contaminant vapor concentrations, and the vapor flowpath relative to the contaminant location. In an article by Johnson et al.[2] simple mathematical equations were presented to help quantify each of these factors. Below we illustrate how to utilize these "screening models" and the information collected during the preliminary site investigation to help determine if in-situ soil venting is appropriate at a given site. In making this decision we will answer the following questions:

(1) *What contaminant vapor concentrations are likely to be obtained?*

(2) *Under ideal vapor flow conditions (i.e. 100 - 1000 scfm vapor flowrates), is this concentration great enough to yield acceptable removal rates?*

(3) *What range of vapor flowrates can realistically be achieved?*

(4) *Will the contaminant concentrations and realistic vapor flowrates produce acceptable removal rates?*

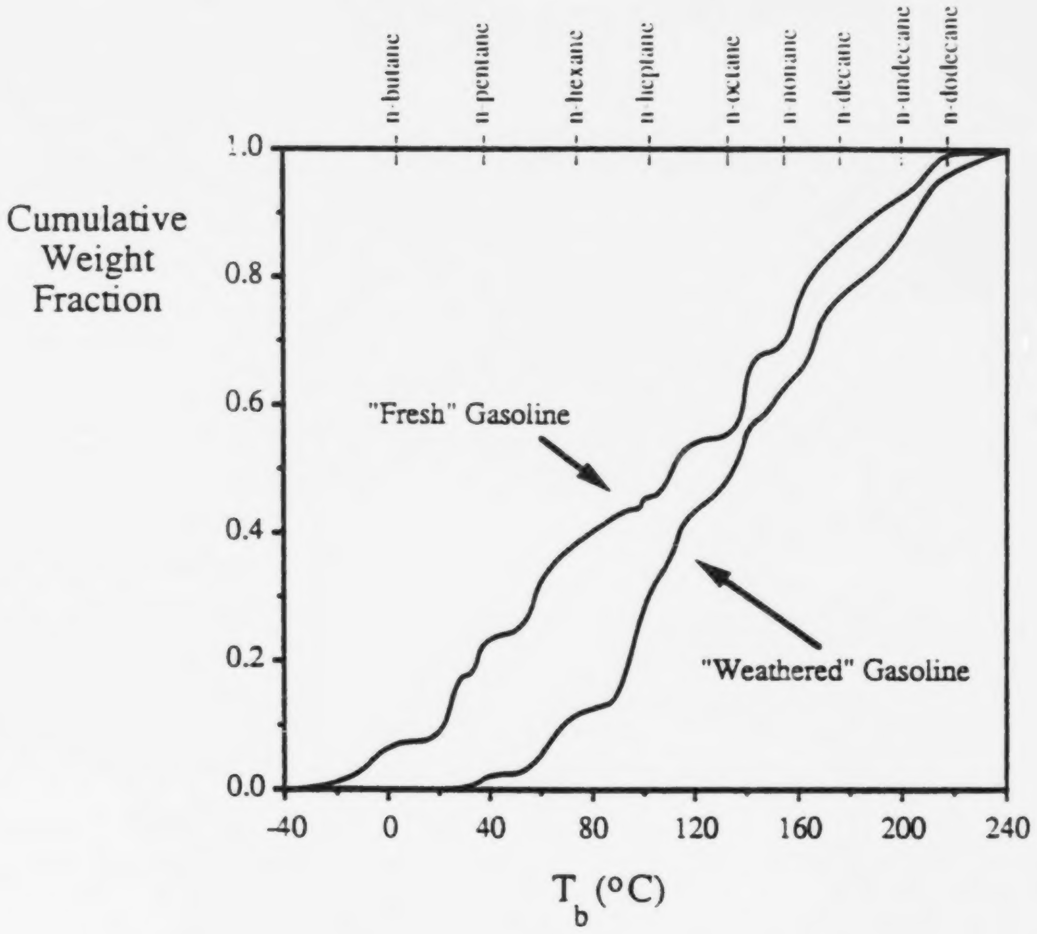

Figure E-3. Boiling Point Distribution Curves for Samples of "Fresh" and "Weathered" Gasolines.

(5) What are the vapor composition and concentration changes? What residual, if any, will be left in the soil?

(6) Are there likely to be any negative effects of soil venting?

Negative answers to questions (2), (3), or (4) will rule out in-situ soil venting as a practical treatment method.

(1) - What contaminant vapor concentrations are likely to be obtained?

Question (1) can be answered based on the results of soil vapor surveys, analyses of headspace vapors above contaminated soil samples, or equilibrium vapor models[2]. In some cases just knowing which compounds are present is sufficient to estimate if venting is feasible. In the absence of soil-vapor survey data, contaminant vapor concentrations can be estimated. The maximum vapor concentration of any compound (mixture) in extracted vapors is its equilibrium or "saturated" vapor concentration, which is easily calculated from knowledge of the compound's (mixture's) molecular weight, vapor pressure at the soil temperature, residual soil contaminant composition, and the ideal gas law:

$$C_{est} = \sum_{i} \frac{x_i P_i^v M_{w,i}}{RT} \qquad \text{(E-1)}$$

where:

C_{est} = estimate of contaminant vapor concentration [mg/l]
x_i = mole fraction of component i in liquid-phase residual ($x_i = 1$ for single compound)
P_i^v = pure component vapor pressure at temperature T [atm]
$M_{w,i}$ = molecular weight of component i [mg/mole]
R = gas constant = 0.0821 l-atm/mole-°K
T = absolute temperature of residual [°K]

Table E-1 presents data for some chemicals and mixtures often spilled in the environment. There are more sophisticated equations for predicting vapor concentrations in soil systems based on equilibrium partitioning arguments, but these require more detailed information (organic carbon content, soil moisture) than is normally available. If a site is chosen for remediation, the residual total hydrocarbons in soil typically exceed 500 mg/kg. In this residual concentration range the majority of hydrocarbons will be present as a separate or "free" phase, the contaminant vapor concentrations become independent of residual concentration (but still depend on composition), and Equation E-1 is applicable[2]. In any case, it should be noted that these are estimates only for vapor concentrations at the start of venting, which is when the removal rates are generally greatest. Contaminant concentrations in the extracted vapors will decline with time due to changes in composition, residual levels, or increased diffusional resistances. These topics are discussed below in more detail.

Table E-1. Selected Compounds and Their Chemical Properties.

Compound	M_w (g/mole)	T_b (1 atm) (°C)	P_v^o (20°C) (atm)	C_{sat} (mg/l)
n-pentane	72.2	36	0.57	1700
n-hexane	86.2	69	0.16	560
trichloroethane	133.4	75	0.132	720
benzene	78.1	80	0.10	320
cyclohexane	84.2	81	0.10	340
trichloroethylene	131.5	87	0.026	140
n-heptane	100.2	98	0.046	190
toluene	92.1	111	0.029	110
tetrachloroethylene	166	121	0.018	130
n-octane	114.2	126	0.014	65
chlorobenzene	113	132	0.012	55
p-xylene	106.2	138	0.0086	37
ethylbenzene	106.2	138	0.0092	40
m-xylene	106.2	139	0.0080	35
o-xylene	106.2	144	0.0066	29
styrene	104.1	145	0.0066	28
n-nonane	128.3	151	0.0042	22.0
n-propylbenzene	120.2	159	0.0033	16
1,2,4 trimethylbenzene	120.2	169	0.0019	9.3
n-decane	142.3	173	0.0013	7.6
DBCP	263	196	0.0011	11
n-undecane	156.3	196	0.0006	3.8
n-dodecane	170.3	216	0.00015	1.1
napthalene	128.2	218	0.00014	0.73
tetraethyllead	323	dec. @200C	0.0002	2.6
gasoline[1]	95	-	0.34	1300
weathered gasoline[2]	111	-	0.049	220

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[1] Corresponds to "fresh" gasoline defined in Table E-2 with boiling point distribution shown in Figure E-3.

[2] Corresponds to "weathered" gasoline defined in Table E-2 with boiling point distribution shown in Figure E-3.

(2) - Under ideal vapor flow conditions (i.e. 100 - 1000 scfm vapor flowrates), is this concentration great enough to yield acceptable removal rates?

Question (2) is answered by multiplying the concentration estimate C_{est}, by a range of reasonable flowrates, Q:

$$R_{est} = C_{est}\,Q \qquad \text{(E-2)}$$

Here R_{est} denotes the estimated removal rate, and C_{est} and Q must be expressed in consistent units. For reference, documented venting operations at service station sites typically report vapor flowrates in the 10 - 100 scfm range[1], although 100 - 1000 scfm flowrates are achievable for very sandy soils or large numbers of extraction wells. At this point in the decision process we are still neglecting that vapor concentrations decrease during venting due to compositional changes and mass transfer resistances. Figure E-4 presents calculated removal rates R_{est} [kg/d] for a range of C_{est} and Q values. C_{est} values are presented in [mg/l] and [ppm_{CH_4}] units, where [ppm_{CH_4}] represents methane-equivalent parts-per-million volume/volume (ppm_v) units. The [ppm_{CH_4}] units are used because field analytical tools that report [ppm_v] values are often calibrated with methane. The [mg/l] and [ppm_{CH_4}] units are related by:

$$[\text{mg/l}] = \frac{[ppm_{CH_4}] * 16000\text{mg-}CH_4\text{/mole-}CH_4 * 10^{-6}}{(0.0821\ \text{l-atm/°K-mole}) * (298\text{K})} \qquad \text{(E-3)}$$

For field instruments calibrated with other compounds (i.e., butane, propane) [ppm_v] values are converted to [mg/l] by replacing the molecular weight of CH_4 in Equation E-3 by the molecular weight [mg/mole] of the calibration compound.

Acceptable or desirable removal rates $R_{acceptable}$, can be determined by dividing the estimated spill mass M_{spill}, by the maximum acceptable clean-up time τ:

$$R_{acceptable} = M_{spill}/\tau \qquad \text{(E-4)}$$

For example, if 1500 kg (≈500 gal) of gasoline had been spilled at a service station and we wished to complete the clean-up within eight months, then $R_{acceptable} = 6.3$ kg/d. Based on Figure E-4, therefore, C_{est} would have to average >1.5 mg/l (2400 ppm_{CH_4}) for Q=2800 l/min (100 cfm) if venting is to be an acceptable option. Generally, removal rates <1 kg/d will be unacceptable for most spills, so soils contaminated with compounds (mixtures) having saturated vapor concentrations less than 0.3 mg/l (450 ppm_{CH_4}) will not be good candidates for venting, unless vapor flowrates exceed 100 scfm. Judging from the compounds listed in Table E-1, this corresponds to compounds with

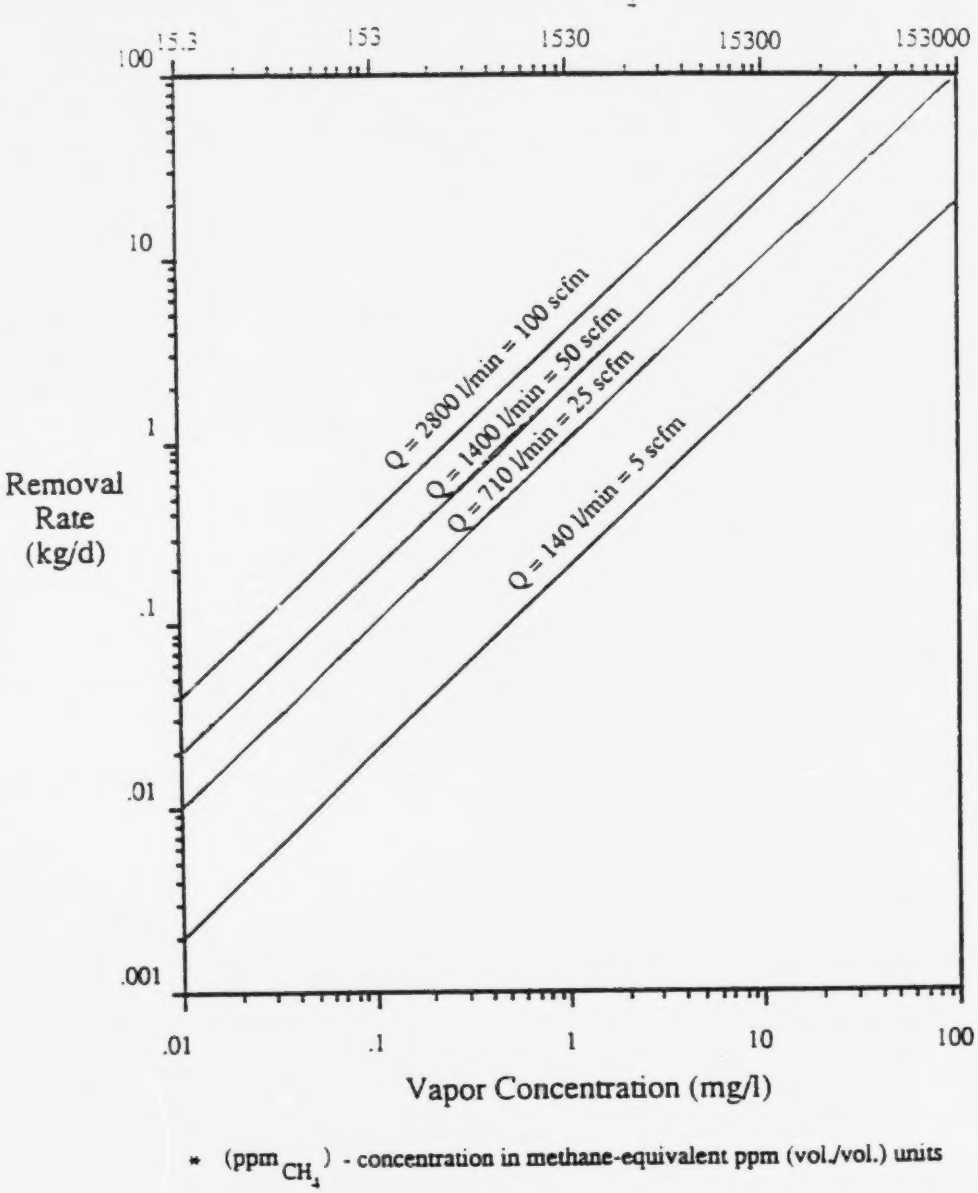


Figure E-4. In-Situ Soil Venting Removal Rate Dependence on Vapor Extraction Rate and Vapor Concentration.

boiling points (T_b)>150°C, or pure component vapor pressures <0.0001 atm evaluated at the subsurface temperature.

- *What range of vapor flowrates can realistically be achieved?*

Question (3) requires that we estimate realistic vapor flowrates for our site specific conditions. Equation E-5, which predicts the flowrate per unit thickness of well screen Q/H [cm^3/s], can be used for this purpose:

$$\frac{Q}{H} = \pi\frac{k}{\mu}P_w \frac{[1-(P_{atm}/P_w)^2]}{\ln(R_w/R_I)} \qquad \text{(E-5)}$$

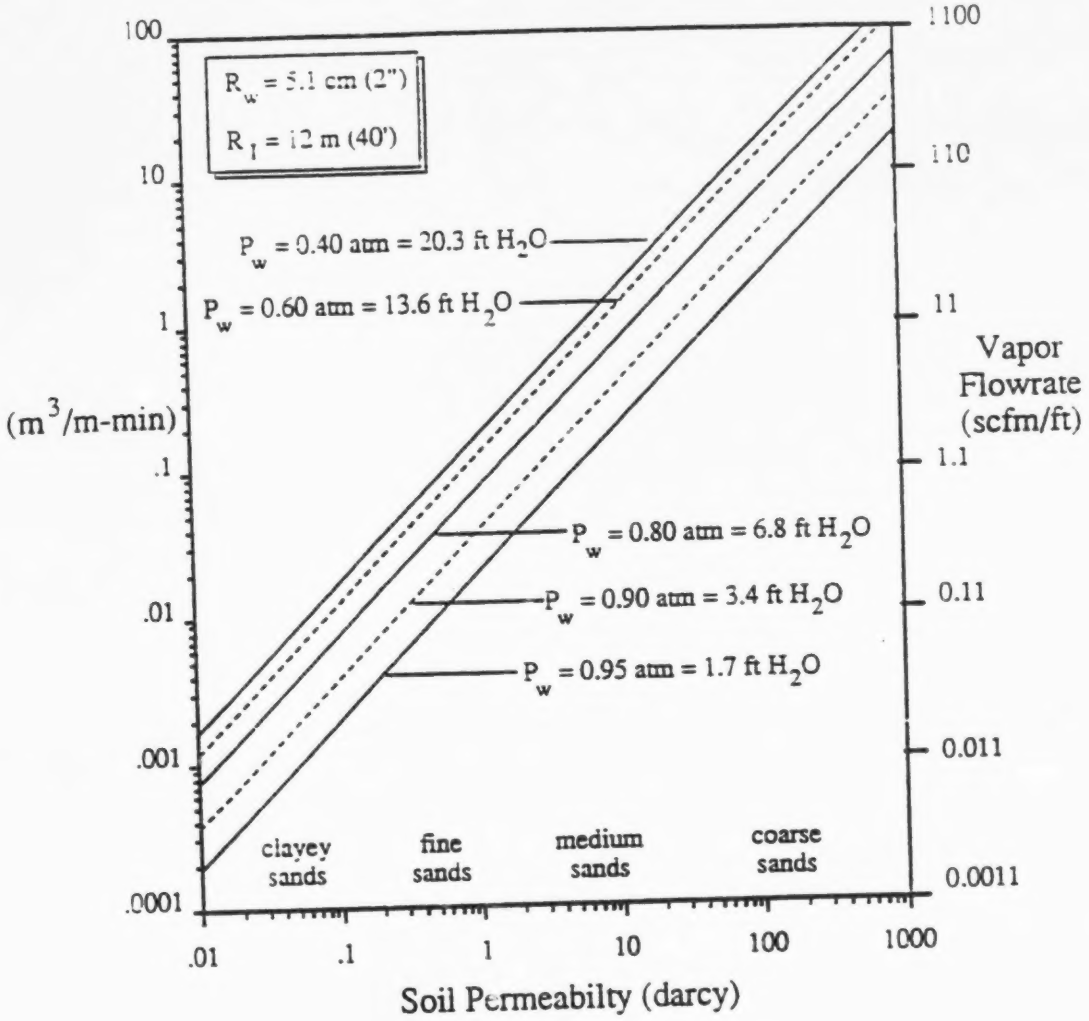
where:

k = soil permeability to air flow [cm^2] or [darcy]
m = viscosity of air = 1.8×10^{-4} g/cm-s or 0.018 cp
P_w = absolute pressure at extraction well [$g/cm\text{-}s^2$] or [atm]
P_{Atm} = absolute ambient pressure ≈ 1.01×10^6 $g/cm\text{-}s^2$ or 1 atm
R_w = radius of vapor extraction well [cm]
R_I = radius of influence of vapor extraction well [cm]

This equation is derived from the simplistic steady-state radial flow solution for compressible flow[2], but should provide reasonable estimates for vapor flowrates. If we can measure or estimate k, then the only unknown parameter is the empirical "radius of influence" R_I. Values ranging from 9 m (30 ft) to 30 m (100 ft) are reported in the literature for a variety of soil conditions, but fortunately Equation E-5 is not very sensitive to large changes in R_I. For estimation purposes, therefore, a value of R_I=12 m (40 ft) can be used without a significant loss of accuracy. Typical vacuum well pressures range from 0.95 - 0.90 atm (20 - 40 in H_2O vacuum). Figure E-5 presents predicted flowrates per unit well screen depth Q/H, expressed in "standard" volumetric units Q*/H (= $Q/H(P_w/P_{Atm})$) for a 5.1 cm radius (4" diameter) extraction well, and a wide range of soil permeabilities and applied vacuums. Here H denotes the thickness of the screened interval, which is often chosen to be equal to the thickness of the zone of soil contamination (this minimizes removing and treating any excess "clean" air). For other conditions the Q*/H values in Figure E-5 can be multiplied by the following factors:

R_w = 5.1 cm (2") R_I = 7.6 m (25') - multiply by Q*/H by 1.09
R_w = 5.1 cm (2") R_I = 23 m (75') - multiply by Q*/H by 0.90
R_w = 7.6 cm (3") R_I = 12 m (40') - multiply by Q*/H by 1.08
R_w = 10 cm (4") R_I = 12 m (40') - multiply by Q*/H by 1.15
R_w = 10 cm (4") R_I = 7.6 m (25') - multiply by Q*/H by 1.27

As indicated by the multipliers given above, changing the radius of influence from 12 m (40 ft) to 23 m (75 ft) only decreases the predicted flowrate by 10%. The largest uncertainty in flowrate calculations will be due to the air permeability value k, which can vary by one to three orders of magnitude across a site and can realistically only be estimated from boring log data



[ft H_2O] denote vacuums expressed as equivalent water column heights

Figure E-5. Predicted Steady-State Flowrates (per unit well screen depth) for a Range of Soil Permeabilities and Applied Vacuums (P_v).

within an order of magnitude. It is prudent, therefore, to choose a range of k values during this phase of the decision process. For example, if boring logs indicate fine sandy soils are present, then flowrates should be calculated for k values in the range $0.1<k<1.0$ darcy.

(4) - Will the contaminant concentrations and realistic vapor flowrates produce acceptable removal rates?

Again, estimated removal rates R_{est}, must be compared with an acceptable rate $R_{acceptable}$, as determined from Equation E-4. Maximum removal rates are achieved when the induced vapor flow travels only through the zone of soil contamination and no mass-transfer limitations are encountered. In other words, all vapor flows through contaminated soils and becomes saturated with contaminant vapors. For this "best" case the estimated removal rate is given by Equation E-2:

$$R_{est} = C_{est}\,Q \qquad \text{(E-2)}$$

We are still neglecting changes in C_{est} with time due to composition changes. Other less optimal conditions are often encountered in practice and it is useful to be able to quantify how much lower the removal rate will be from the value predicted by Equation E-2. We will consider the three cases illustrated in Figure E-6a, b, and c.

In Figure E-6a, a fraction ϕ of the vapor flows through uncontaminated soil. The fraction can be roughly estimated by assessing the location of the well relative the contaminant distribution. In Figure E-6a, for example, it appears that roughly 25% of the vapor flows through uncontaminated soil. The maximum removal rate for this case is then:

$$R_{est} = (1-\phi)Q\,C_{est} \qquad \text{(E-6)}$$

In Figure E-6b, vapor flows parallel to, but not through, the zone of contamination, and the significant mass transfer resistance is vapor phase diffusion. This would be the case for a layer of liquid hydrocarbon resting on top of an impermeable strata or the water table. This problem was studied by Johnson et al.[2] for the case of a single component. Their solution is:

$$R_{est} = \eta Q C_{est}$$

$$\eta = \frac{1}{3H}(6D\mu/\kappa)^{1/2}[\ln(R_I/R_v)/(P_{Atm}-P_v)]^{1/2}\ [R_2{}^2-R_1{}^2]^{1/2} \qquad \text{(E-7)}$$

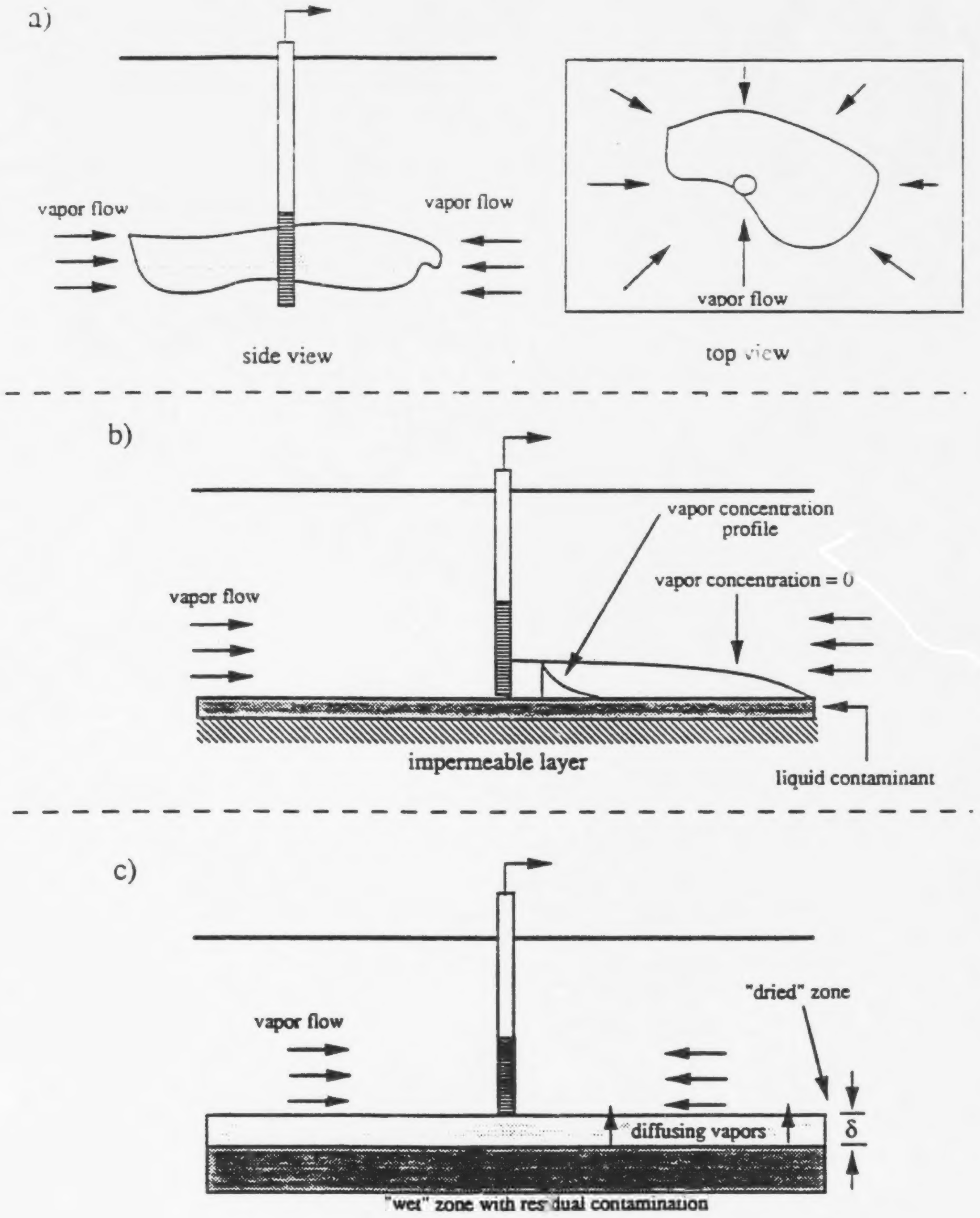

a)
vapor flow
vapor flow
side view
vapor flow
top view
b)
vapor concentration profile
vapor concentration = 0
vapor flow
impermeable layer
liquid contaminant
c)
"dried" zone
vapor flow
diffusing vapors
δ
"wet" zone with residual contamination

Figure E-6. Scenarios for Removal Rate Estimates.

where:

η = efficiency relative to maximum removal rate
D = effective soil vapor diffusion coefficient [cm^2/s]
μ = viscosity of air = 1.8×10^{-4} g/cm-s
k = soil permeability to vapor flow [cm^2]
H = thickness of screened interval [cm]
R_I = radius of influence of venting well [cm]
R_w = venting well radius [cm]
P_{Atm} = absolute ambient pressure = 1.016×10^6 g/cm-s^2
P_w = absolute pressure at the venting well [g/cm-s^2]
$R_1<r<R_2$ = defines region in which contamination is present

Note that the efficiency η is inversely proportional to the screened interval thickness H because a larger interval will, in this geometry, pull in unsaturated air that has passed above the liquid-phase contamination. D is calculated by the Millington-Quirk[3] expression, which utilizes the molecular diffusion coefficient in air D°, the vapor-filled soil porosity ϵ_A, and the total soil porosity ϵ_T:

$$D = D^{\circ} \frac{\epsilon_A^{3.33}}{\epsilon_t^{2}} \qquad \text{(E-8)}$$

where ϵ_A and ϵ_t are related by:

$$\epsilon_A = \epsilon_t - \rho_b \theta_M \qquad \text{(E-9)}$$

Here ρ_b and θ_M are the soil bulk density [g/cm^3] and soil moisture content [g-H_2O/g-soil].

As an example, consider removing a layer of contamination bounded by sandy soil (k=1 darcy). A 5.1-cm (2") radius extraction well is being operated at P_w=0.90 atm (0.91×10^6 g/cm-s^2), and the contamination extends from the region $R_1 = R_w = 5.1$ cm to $R_2 = 9$ m (30 ft). The well is screened over a 3m (10 ft) interval. Assuming that:

ρ_b = 1.6 g/cm^3
θ_M = 0.10
D° = 0.087 cm^2/s
ϵ_T = 0.30
R_I = 12 m

then the venting efficiency relative to the maximum removal rate (Equation E-5), calculated from Equations E-7 through E-9 is:

$$\eta = 0.09 = 9\%$$

Figure E-6c depicts the situation in which vapor flows primarily past, rather than through the contaminated soil zone, such as might be the case for a contaminated clay lens surrounded by sandy soils. In this case vapor phase diffusion through the clay to the flowing vapor limits the removal rate. The maximum removal rate in this case occurs when the vapor flow is fast enough to maintain a very low vapor concentration at the permeable/impermeable soil interface. At any time t a contaminant-free or "dried out" zone of low permeability will exist with a thickness δ. An estimate of the removal rate R_{est} from a contaminated zone extending from R_1 to R_2 is:

$$R_{est} = \pi(R_2^2 - R_1^2)C_{est}D/\delta(t) \tag{E-10}$$

where D is the effective porous media vapor diffusion coefficient (as calculated above from Equations E-8 and E-9) and C_{est} is the estimated equilibrium vapor concentration (Equation E-1). With time $\delta(t)$ will grow larger. In the case of a single component system the dry zone thickness can be calculated from the mass balance:

$$\rho_b C_s \frac{d\delta}{dt} = C_{est}D/\delta(\tau) \tag{E-11}$$

where C_s is the residual level of contamination in the low permeability zone [g-contamination/g-soil], and all other variables are defined above. The solution to Equations E-10 and E-11 yields the following equation that predicts the change in removal rate with time:

$$\delta(\tau) = \frac{[2C_{est}Dt]^{1/2}}{\rho_b C_s}$$

$$R_{est} = \pi(R_2^2 - R_1^2)\frac{[C_{est}DC_s\rho_b]^{1/2}}{2\tau} \tag{E-12}$$

As an example, consider the case where benzene ($C_v = 3.19 \times 10^{-4}$ g/cm^3 @20°C) is being removed from a zone extending from $R_1 = 5.1$ cm to $R_2 = 9$ m. The initial residual level is 10,000 ppm (0.01 g-benzene/g-soil), $\rho_b = 1.6$ g/cm^3, $D^\circ = 0.087$ cm^2/s, and $\epsilon_T = \epsilon_A = 0.30$. Figure E-7 presents the predicted removal rates and "dry" zone thickness d(t) as a function of time. Note that it would take approximately one year to clean a layer 1.5 m (5 ft) thick, for a compound as volatile as benzene. Equation E-12 predicts very high initial removal rates; in practice, however, the removal rate will be limited initially by the vapor-phase diffusion behavior described above for Figure E-6b.

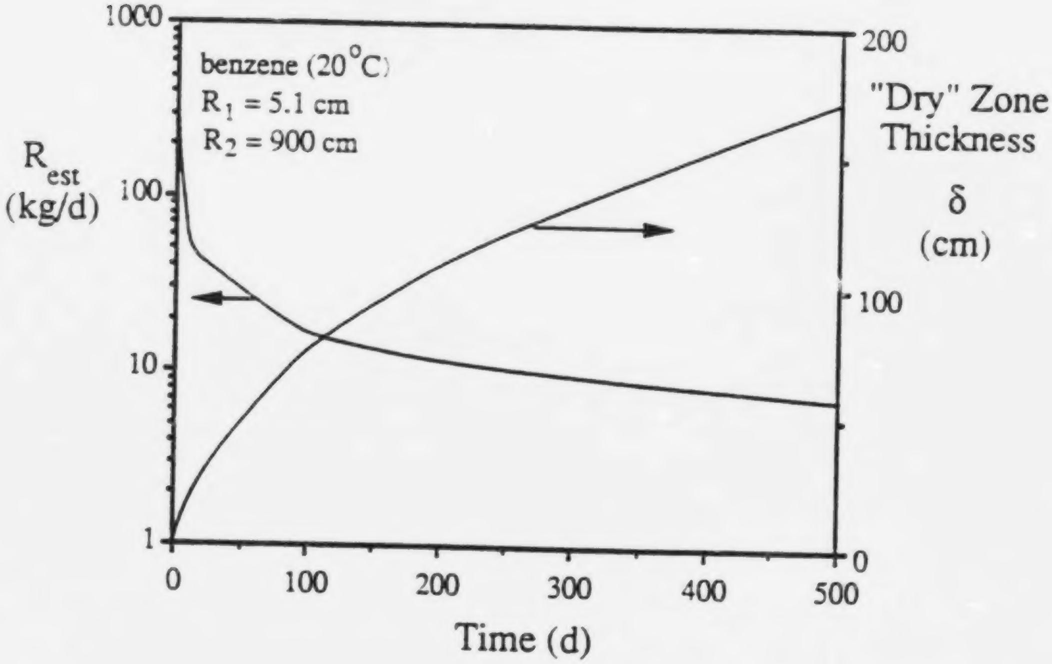


Figure E-7. Estimated Maximum Removal Rates for a Venting Operation Limited by Diffusion.

Mixture removal rates for the situations depicted in Figures E-6b and E-6c are difficult to estimate because changes in composition and liquid-phase diffusion affect the behavior. Presently there are no simple analytical solutions for these situations, but we can postulate that they should be less than the rates predicted above for pure components.

The use of equilibrium-based models to predict required removal rates is discussed below under the next question.

(5) - What are the vapor composition and concentration changes? What residual, if any, will be left in the soil?

As contaminants are removed during venting, the residual soil contamination level decreases and mixture compositions become richer in the less volatile compounds. Both of these processes result in decreased vapor concentrations, and hence, decreased removal rates with time. At low residual soil contamination levels (<500 ppm) Equation E-1 becomes less valid as sorption and dissolution phenomena begin to affect the soil residual - vapor equilibrium. In the limit of low residual contamination levels, contaminant equilibrium vapor concentrations are expected to become proportional to the residual soil contaminant concentrations. As venting continues and residual soil levels decrease, therefore, it becomes more difficult to remove the residual contamination. It is important to realize that, even with soil venting, there are practical limitations on the final soil contamination levels that can be achieved. Knowledge of these limits is necessary to realistically set clean-up criteria and design effective venting systems.

The maximum efficiency of a venting operation is limited by the equilibrium partitioning of contaminants between the soil matrix and vapor phases. The maximum removal rate is achieved when the vapor being removed from an extraction well is in equilibrium with the contaminated soil. Models for predicting this maximum removal rate have been presented by Marley and Hoag[4] and Johnson et al.[2] The former considered only compositions in a residual free-phase, while the latter also considered the effects of sorption and dissolution processes. A complete discussion of the development of these models is not appropriate here, but we will discuss use of the predictions.

The change in composition, vapor concentration, removal rate, and residual soil contamination level with time are functions of the initial residual composition, vapor extraction well flowrate, and initial soil contamination level. It is not necessary to generate predictions for every combination of variables, however, because with appropriate scaling all results will form a single curve for a given initial mixture composition. Figure E-8a presents the results computed with the model presented by Johnson et al.[2] for the "weathered" gasoline mixture whose composition is given by Table E-2. The important variable that determines residual soil levels, vapor concentrations, and removal rates is the ratio $Qt/M(t=0)$, which represents the volume of air drawn through the contaminated zone per unit mass of contaminant. In Figure E-8, the scaled removal rate (or equivalently the

Table E-2. Composition of "Fresh" and "Weathered" Gasolines.

Compound Name	Mw (g)	Fresh Gasoline	Weathered Gasoline	Approximate Composition
propane	44.1	0.0001	0.0000	0
isobutane	58.1	0.0122	0.0000	0
n-butane	58.1	0.0629	0.0000	0
trans-2-butene	56.1	0.0007	0.0000	0
cis-2-butene	56.1	0.0000	0.0000	0
3-methyl-1-butene	70.1	0.0006	0.0000	0
isopentane	72.2	0.1049	0.0000	0
1-pentene	70.1	0.0000	0.0069	0.0177
2-methyl-1-butene	70.1	0.0000	0.0005	0
2-methyl-1,3-butadiene	68.1	0.0000	0.0008	0
n-pentane	72.2	0.0586	0.0000	0
trans-2-pentene	70.1	0.0000	0.0095	0
2-methyl-2-butene	70.1	0.0044	0.0017	0
3-methyl-1,2-butadiene	68.1	0.0000	0.0021	0
3,3-dimethyl-1-butene	84.2	0.0049	0.0010	0
cyclopentane	70.1	0.0000	0.0000	0
3-methyl-1-pentene	84.2	0.0000	0.0046	0.0738
2,3-dimethylbutane	86.2	0.0730	0.0000	0
2-methylpentane	86.2	0.0273	0.0044	0
3-methylpentane	86.2	0.0000	0.0207	0
n-hexane	86.2	0.0283	0.0186	0
methylcyclopentane	84.2	0.0083	0.0207	0
2,2-dimethylpentane	100.2	0.0076	0.0234	0
benzene	78.1	0.0076	0.0064	0
cyclohexane	84.2	0.0000	0.0021	0
2,3-dimethylpentane	100.2	0.0390	0.0137	0.1761
3-methylhexane	100.2	0.0000	0.0000	0
3-ethylpentane	100.2	0.0000	0.0355	0
n-heptane	100.2	0.0063	0.0000	0
2,2,4-trimethylpentane	114.2	0.0121	0.0447	0
methylcyclohexane	98.2	0.0000	0.0503	0
2,2-dimethylhexane	114.2	0.0055	0.0393	0
toluene	92.1	0.0550	0.0207	0
2,3,4-trimethylpentane	114.2	0.0121	0.0359	0.1926
3-methylheptane	114.2	0.0000	0.0000	0
2-methylheptane	114.2	0.0155	0.0343	0
n-octane	114.2	0.0013	0.0324	0

Table E-2 (continued). Composition of "Fresh" and "Weathered" Gasolines.

2,4,4-trimethylhexane	128.3	0.0087	0.0034	0
2,2-dimethylheptane	128.3	0.0000	0.0226	0
ethylbenzene	106.2	0.0000	0.0130	0
p-xylene	106.2	0.0957	0.0151	0
m-xylene	106.2	0.0000	0.0376	0.1641
3,3,4-trimethylhexane	128.3	0.0281	0.0056	0
o-xylene	106.2	0.0000	0.0274	0
2,2,4-trimethylheptane	142.3	0.0105	0.0012	0
n-nonane	128.3	0.0000	0.0382	0
3,3,5-trimethylheptane	142.3	0.0000	0.0000	0
n-propylbenzene	120.2	0.0841	0.0117	0.1455
2,3,4-trimethylheptane	142.3	0.0000	0.0000	0
1,3,5-trimethylbenzene	120.2	0.0411	0.0493	0
1,2,4-trimethylbenzene	120.2	0.0213	0.0705	0
n-decane	142.3	0.0000	0.0140	0
methylpropylbenzene	134.2	0.0351	0.0170	0
dimethylethylbenzene	134.2	0.0307	0.0289	0.0534
n-undecane	156.3	0.0000	0.0075	0
1,2,4,5-tetramethylbenzene	134.2	0.0133	0.0056	0
1,2,3,4-tetramethylbenzene	134.2	0.0129	0.0704	0.1411
1,2,4-trimethyl-5-ethylbenzene	148.2	0.0405	0.0651	0
n-dodecane	170.3	0.0230	0.0000	0
napthalene	128.2	0.0045	0.0076	0
n-hexylbenzene	162.3	0.0000	0.0147	0.0357
methylnapthalene	142.2	0.0023	0.0134	0
Total		1.0000	1.0000	1.0000

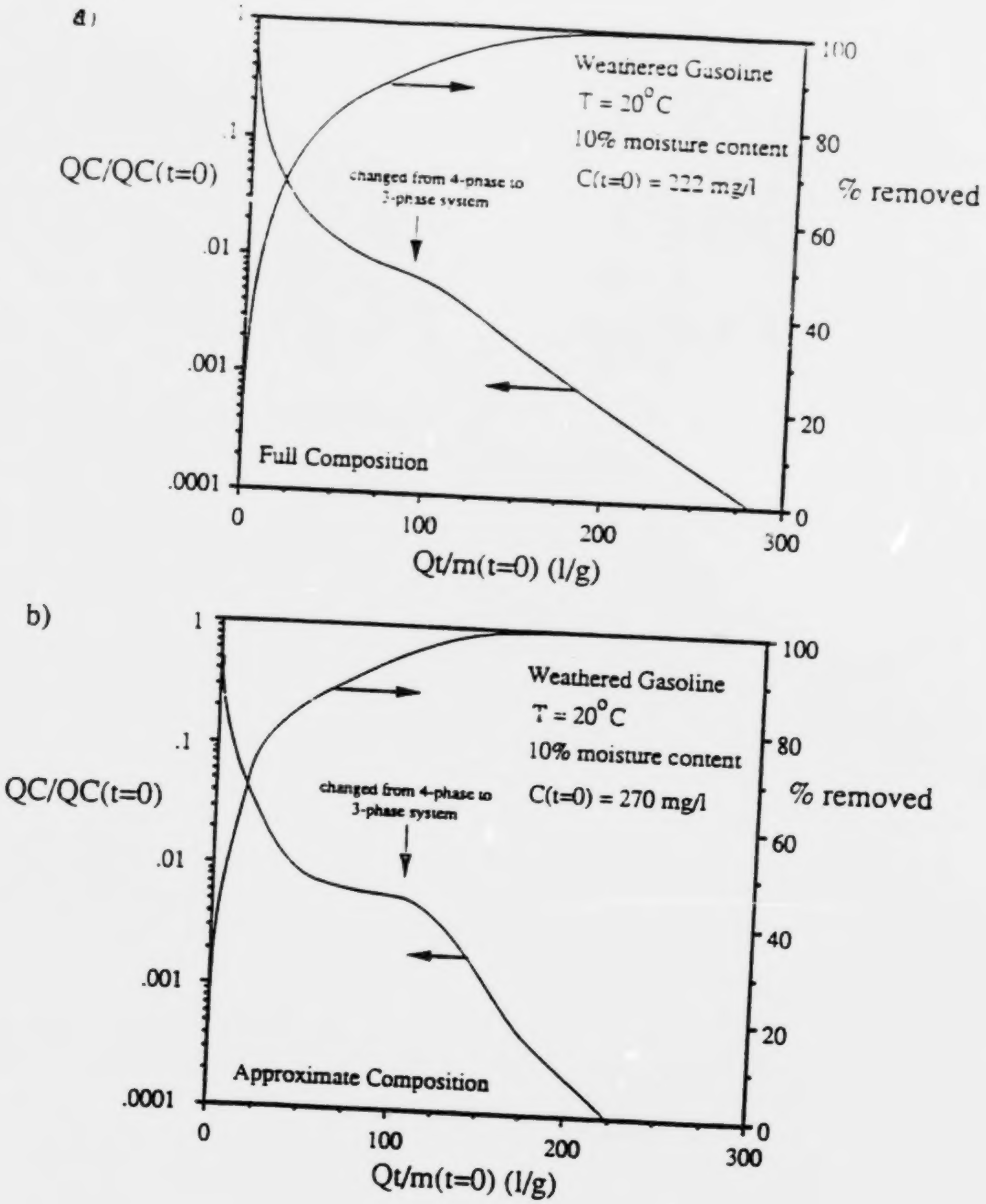


Figure E-8. Maximum Predicted Removal Rates for a Weathered Gasoline. a) full composition, b) approximate composition.

vapor concentration) decreases with time as the mixture becomes richer in the less volatile compounds.

While a detailed compositional analysis was available for this gasoline sample, an approximate composition based on a boiling point distribution curve predicts similar results. Figure E-8b presents the results for the approximate mixture composition also given in Table E-2.

Model predictions, such as those shown in Figure E-8 for the gasoline sample defined by Table E-2, can be used to estimate removal rates (if the vapor flowrate is specified), or alternatively the predictions can be used to estimate vapor flowrate requirements (if the desired removal rate is specified). For example, if we wanted to reduce the initial contamination level by 90%, then Figure E-8 predicts that ≈100 l-air/g-gasoline will be required. This is the minimum amount of vapor required, because it is based on an equilibrium-based model. The necessary minimum average vapor flowrate is then equal to the spill mass times the minimum required vapor flow/mass gasoline divided by the desired duration of venting. Use of this approach is illustrated in the service station site example provided at the end of this paper.

Figure E-8 also illustrates that there is a practical limit to the amount of residual contaminant that can be removed by venting alone. For example, it will take a minimum of 100 l-vapor/g-gasoline to remove 90% of the weathered gasoline defined in Table E-2, while it will take about 200 l-air/g-gasoline to remove the remaining 10%. In the case of gasoline, by the time 90% of the initial residual has been removed the residual consists of relatively insoluble and nonvolatile compounds. It is important to recognize this limitation of venting, and when setting realistic clean-up target levels, they should be based on the potential environmental impact of the residual rather than any specific total residual hydrocarbon levels.

(6) - Are there likely to be any negative effects of soil venting?

It is possible that venting will induce the migration of off-site contaminant vapors towards the extraction wells. This is likely to occur at a service station, which is often in close proximity to other service stations. If this occurs, one could spend a lot of time and money to unknowingly clean-up someone else's problem. The solution is to establish a "vapor barrier" at the perimeter of the contaminated zone. This can be accomplished by allowing vapor flow into any perimeter groundwater monitoring wells, which then act as passive air supply wells. In other cases it may be necessary to install passive air injection wells, or trenches, as illustrated in Figure E-9a.

As pointed out by Johnson et al.[2] the application of a vacuum to extraction wells can also cause a water table rise. In many cases contaminated soils lie just above the water table and they become water saturated, as illustrated in Figure E-9b. The maximum rise occurs at the vapor extraction well, where the water table rise will be equal to the vacuum

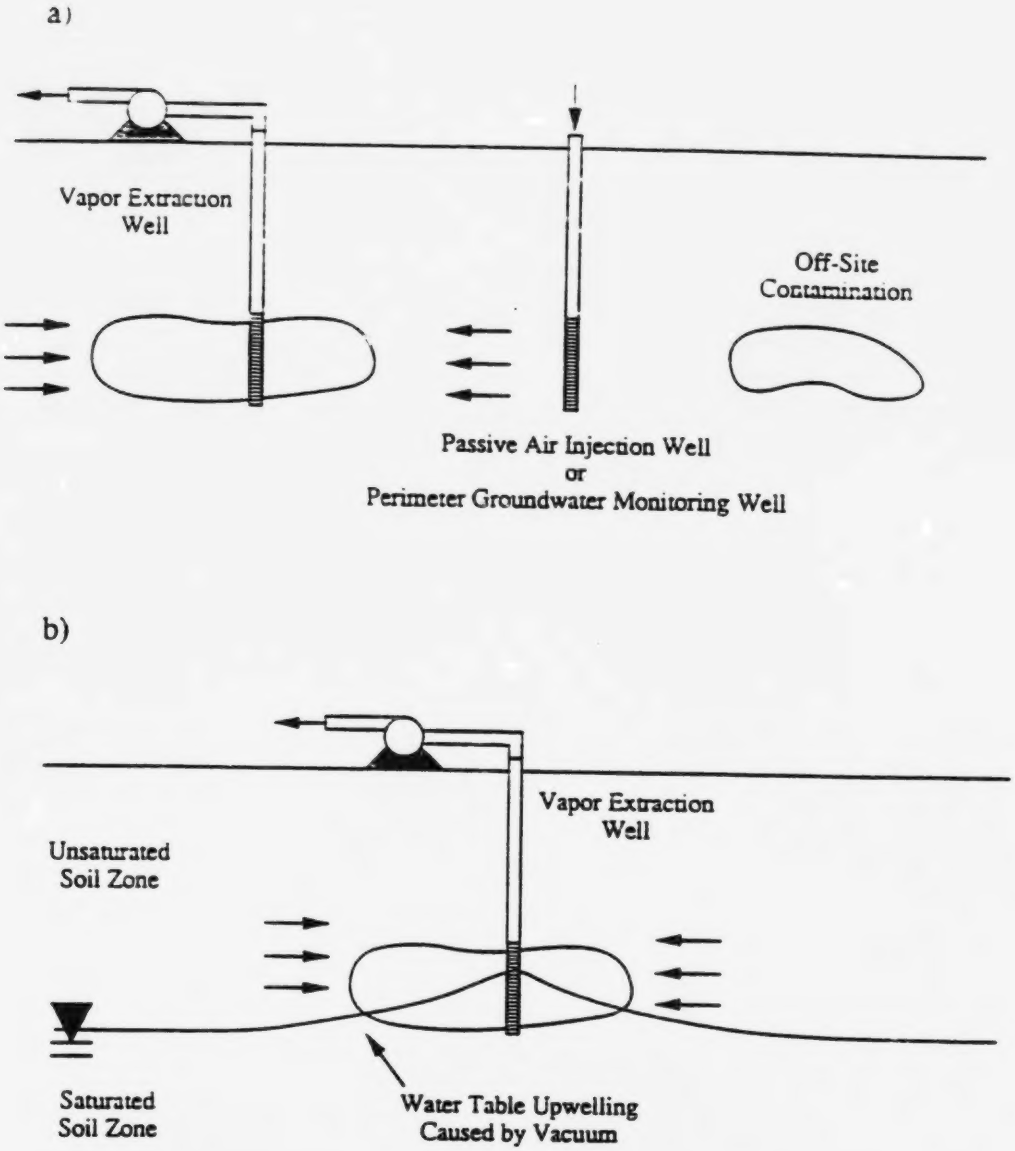

a)
Vapor Extraction Well
Off-Site Contamination
Passive Air Injection Well or Perimeter Groundwater Monitoring Well
b)
Vapor Extraction Well
Unsaturated Soil Zone
Saturated Soil Zone
Water Table Upwelling Caused by Vacuum

Figure E-9. a) Use of Passive Vapor Wells to Prevent Migration of Off-Site Contaminant Vapors. b) Water Table Rise Caused by the Applied Vacuum.

at the well expressed as an equivalent water column height (i.e., in or ft H_2O). The solution to this problem is to install a dewatering system, with groundwater pumping wells located as close to vapor extraction wells as possible. The dewatering system must be designed to insure that contaminated soils remain exposed to vapor flow. Other considerations not directly related to venting system design, such as soluble plume migration control and free-liquid product yield, will also be factors in the design of groundwater pumping system.

Design Information

If venting is still a remediation option after answering the questions above, then more accurate information must be collected. Specifically, the soil permeability to vapor flow, vapor concentrations, and aquifer characterics are required. These are obtained by two field experiments: air permeability and groundwater pump tests. These are described briefly below.

Air Permeability Tests

Figure E-10 depicts the set-up of an air permeability test. The object of this experiment is to remove vapors at a constant rate from an extraction well, while monitoring with time the transient subsurface pressure distribution at fixed points. Effluent vapor concentrations are also monitored. It is important that the test be conducted properly to obtain accurate design information. The extraction well should be screened through the soil zone that will be vented during the actual operation. In many cases existing groundwater monitoring wells are sufficient, if their screened sections extend above the water table. Subsurface pressure monitoring probes can be driven soil vapor sampling probes (for shallow <20 ft deep contamination problems) or more permanent installations.

Flowrate and transient pressure distribution data are used to estimate the soil permeability to vapor flow. The expected change in the subsurface pressure distribution with time P'(r,t) is predicted[2] by:

$$P' = \frac{Q}{4\pi m(k/\mu)} \int_{\frac{r^2 \epsilon\mu}{4kP_{Atm}t}}^{\infty} \frac{e^{-x}}{x}\, dx \qquad \text{(E-13)}$$

For $(r^2 /4kP_{Atm}t)<0.1$ Equation E-13 can be approximated by:

$$P' = \frac{Q}{4\pi m(k/\mu)}\left[-0.5772 - \ln\left(\frac{r^2 \epsilon\mu}{4kP_{Atm}}\right) + \ln(t)\right] \qquad \text{(E-14)}$$

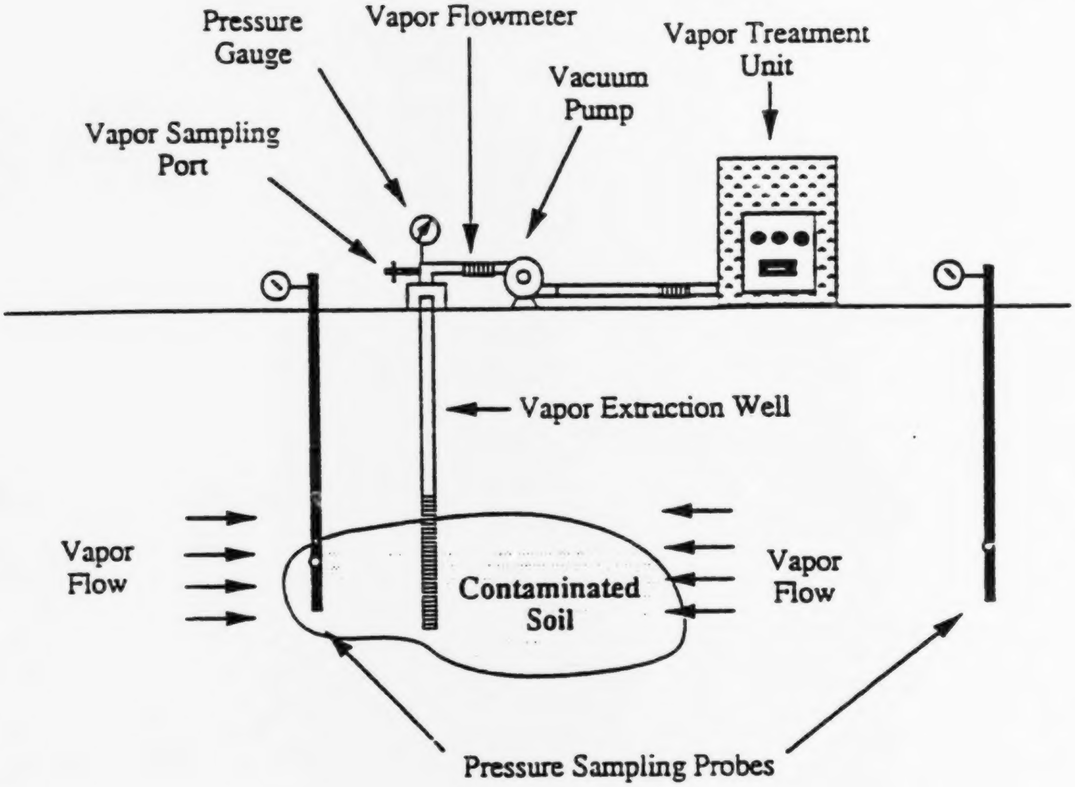

Pressure Gauge
Vapor Flowmeter
Vapor Treatment Unit
Vacuum Pump
Vapor Sampling Port
Vapor Extraction Well
Vapor Flow
Contaminated Soil
Vapor Flow
Pressure Sampling Probes

Figure E-10. Air Permeability Test System.

where:

P' - "gauge" pressure measured at distance r and time t
m - stratum thickness
r - radial distance from vapor extraction well
k - soil permeability to air flow
μ - viscosity of air = 1.8×10^{-4} g/cm-s
ϵ - air-filled soil void fraction
t - time
Q - volumetric vapor flowrate from extraction well
P_{Atm} - ambient atmospheric pressure = 1.0 atm = 1.013×10^{6} g/cm-s^2

Equation E-14 predicts that a plot of P' -vs- ln(t) should be a straight line with slope A and y-intercept B equal to:

$$A = \frac{Q}{4\pi m(k/\mu)} \quad B = \frac{Q}{4\pi m(k/\mu)}\left[-0.5772 - \ln\left(\frac{r^2\epsilon\mu}{4kP_{Atm}}\right)\right] \tag{E-15}$$

The permeability to vapor flow can then be calculated from the data by one of two methods. The first is applicable when Q and m are known. The calculated slope A is used:

$$k = \frac{Q\mu}{4A\pi m} \tag{E-16}$$

The second approach must be used whenever Q or m is not known. In this case the values A and B are both used:

$$k = \frac{r^2\epsilon\mu}{4P_{Atm}}\exp\left(\frac{B}{A} + 0.5772\right) \tag{E-17}$$

Equation E-13 can also be used to choose the locations of subsurface pressure monitoring points before conducting the air permeability test, given an estimation of k and the flowrate to be used.

Vapor samples should be taken at the beginning and end of the air permeability test, which should be conducted for a long enough time to extract at least one "pore volume" V_P of vapor from the contaminated soil zone. This insures that all vapors existing in the formation prior to venting are removed. The vapor concentration at the start of the test is representative of the equilibrium vapor concentration, while the concentration measured after one pore volume has been extracted gives an indication of realistic removal rates and the mixing or diffusional limitations discussed in association with Figure E-6. The time τ_P for one pore volume to be removed is:

$$\tau_P = V_P/Q = \epsilon_A \pi R^2 H/Q \tag{E-18}$$

where R, H, ϵ_A, and Q are the radius of the zone of contamination, vertical thickness of the zone of contamination, air-filled void fraction, and volumetric vapor flowrate from the extraction well. For example, consider the case where R=12 m, H=3 m, ϵ_A=0.35, and Q=0.57 m^3/min (20 ft^3/min). Then τ_p=475 m^3/0.57 m^3/min=833 min=14 h.

Groundwater Pump Tests

To achieve efficient venting the hydrocarbon-contaminated soil has to be exposed to air flow, which in turn requires that the water table be lowered to counteract the water upwelling effect caused by the decreased vapor pressure in the vicinity of a venting well (Johnson et al.[2]) and to possibly expose contaminated soil below the water table. Thus the groundwater pumping system has to have a sufficient pumping rate and be operated for a long enough time period to obtain the required drawdowns. Since most venting systems are installed above phreatic aquifers, two aquifer parameters are needed for the design: average transmissivity T and effective porosity S. These parameters can be estimated using the results of the standard transient groundwater pump test with a constant pumping rate (Bear[5]). Using the estimated values the required pumping rate may be calculated as follows:

$$Q = 4\pi TS(r,t)/W(u) \qquad \text{(E-19)}$$

where: W(u) is the well function[5] of $u = Sr^2/4Tt$, and s(r,t) is the required drawdown at distance r and pumping time equal to t.

System Design

In this section we discuss the questions that must be answered in order to design an in-situ soil venting system. It is not our intention to provide a generic "recipe" for soil venting systems design; instead we suggest a structured thought process to guide in choosing the number of extraction wells, well spacing, construction, etc. Even in a structured thought process, intuition and experience play important roles. There is no substitute for a good fundamental understanding of vapor flow processes, transport phenomena, and groundwater flow.

- *Choosing the number of vapor extraction wells*

Three methods for choosing the number of vapor extraction wells are outlined below. The greatest number of wells from these three methods is then the value that should be used. The objective is to satisfy removal rate requirements and achieve vapor removal from the entire zone of contamination.

For the first estimate we neglect residual contaminant composition and vapor concentration changes with time. The acceptable removal rate $R_{acceptable}$ is calculated from Equation E-4, while the estimated removal rate from a single well R_{est} is estimated from a choice of Equations E-2, E-6, E-7, or E-

12 depending on whether the specific site conditions are most like Figure E-6a, E-6b, or E-6c. The number of wells N_{well} required to achieve the acceptable removal rate is:

$$N_{well} = R_{acceptable}/R_{est} \qquad \text{(E-20)}$$

Equations E-2, E-6, and E-7 require vapor flow estimates, which can be calculated from Equation E-5 using the measured soil permeability and chosen extraction well vacuum P_v. At this point one must determine what blowers and vacuum pumps are available because the characteristics of these units will limit the range of feasible (P_v,Q) values. For example, a blower that can pump 100 scfm at 2 in H_2O vacuum may only be able to pump 10 scfm at 100 in H_2O vacuum.

The second method, which accounts for composition changes with time, utilizes model predictions, such as those illustrated in Figure E-8. Recall that equilibrium-based models are used to calculate the minimum vapor flow to achieve a given degree of remediation. For example, if we wish to obtain a 90% reduction in residual gasoline levels, Figure E-8 indicates that ≈100 l-vapor/g-gasoline must pass through the contaminated soil zone. If our spill mass is 1500 kg (~500 gal), then a minimum of 1.5 x 10^8 l-vapor must pass through the contaminated soil zone. If our target clean-up period is six months, this corresponds to a minimum average vapor flowrate of 0.57 m^3/min (~20 cfm). The minimum number of extraction wells is then equal to the required minimum average flowrate/flowrate per well.

The third method for determining the number of wells insures that we remove vapors and residual soil contamination from the entire zone of contamination N_{min}. This is simply equal to the ratio of the area of contamination $A_{contamination}$, to the area of influence of a single venting well $\pi R_I 2$:

$$N_{min} = \frac{A_{contamination}}{\pi R_I^2} \qquad \text{(E-21)}$$

This requires an estimate of R_I, which defines the zone in which vapor flow is induced. In general, R_I depends on soil properties of the vented zone, properties of surrounding soil layers, the depth at which the well is screened, and the presence of any impermeable boundaries (water table, clay layers, surface seal, building basement, etc.). At this point it is useful to have some understanding of vapor flow patterns because, except for certain ideal cases[6], one cannot accurately predict vapor flowpaths without numerically solving vapor flow equations. An estimate for R_I can be obtained by fitting radial pressure distribution data from the air permeability test to the steady-state radial pressure distribution equation[2]:

$$P(r) = P_w\left[1+\left(1-\left(\frac{P_{Atm}}{P_w}\right)^2\right)\frac{\ln(r/R_w)}{\ln(R_w/R_I)}\right]^{1/2} \qquad (E\text{-}22)$$

where $P(r)$, P_{Atm}, P_w, and R_w are the absolute pressure measured at a distance r from the venting well, absolute ambient pressure, absolute pressure applied at the vapor extraction well, and extraction well radius, respectively. Given that these tests are usually conducted for less than a day, the results will generally underestimate R_I. If no site specific data is available, one can conservatively estimate R_I based on the published reports from in-situ soil venting operations. Reported R_I values for permeable soils (sandy soils) at depths greater than 20 ft below ground surface, or shallower soils beneath good surface seals, are usually 10 m - 40 m.[1] For less permeable soils (silts, clays), or more shallow zones R_I is usually less.

- *Choosing well location, spacing, passive wells, and surface seals*

To be able to successfully locate extraction wells, passive wells, and surface seals one must have a good understanding of vapor flow behavior. We would like to place wells so that we insure adequate vapor flow through the contaminated zone, while minimizing vapor flow through other zones.

If one well is sufficient, it will almost always be placed in the geometric center of the contaminated soil zone, unless it is expected that vapor flow channeling along a preferred direction will occur. In that case the well will be placed so as to maximize air flow through the contaminated zone.

When multiple wells are used it is important to consider the effect that each well has on the vapor flow to all other wells. For example, if three extraction wells are required at a given site, and they are installed in the triplate design shown in Figure E-11a, there would be a "stagnant" region in the middle of the wells where air flow would be very small in comparison to the flow induced outside the triplate pattern boundaries. This problem can be alleviated by the use of "passive wells" or "forced injection" wells as illustrated in Figure E-11b (it can also be minimized by changing the vapor flowrates from each well with time). A passive well is simply a well that is open to the atmosphere; in many cases groundwater monitoring wells are suitable. If a passive or forced injection well is to have any positive effect, it must be located within the extraction well's zone of influence. Forced injection wells are simply vapor wells into which air is pumped rather than removed. One must be very careful in choosing the locations of forced injection wells so that contaminant vapors are captured by the extraction wells, rather than forced off-site. To date there have not been any detailed reports of venting operations designed to study the advantages/disadvantages of using forced injection wells. Figure E-11c presents another possible extraction/injection well combination. As illustrated in Figure E-9, passive wells can also be used as vapor barriers to prevent on-site migration of off-site contamination problems.

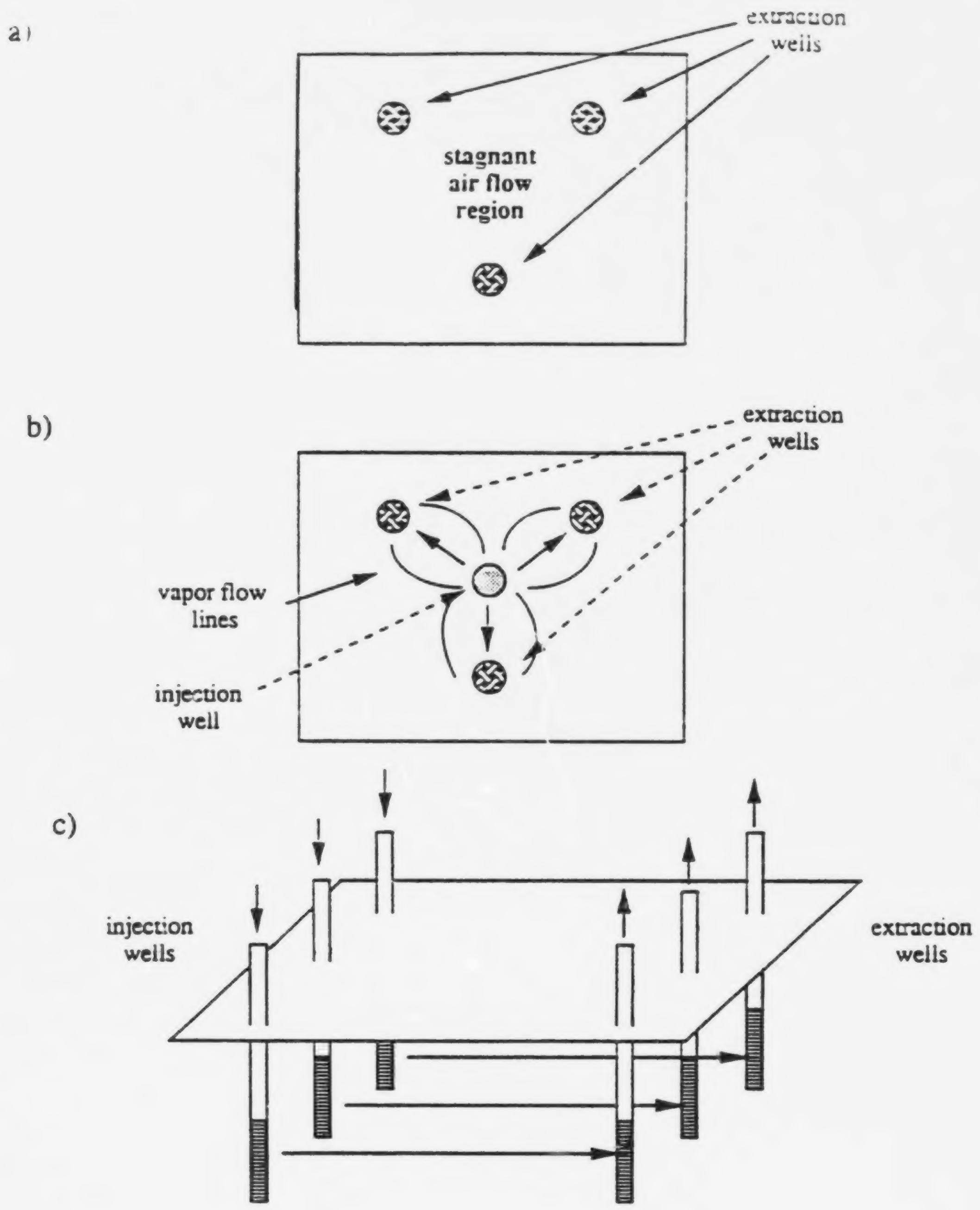

a)
extraction wells
stagnant air flow region
b)
extraction wells
vapor flow lines
injection well
c)
injection wells
extraction wells

Figure E-11. Venting Well Configuration.

For shallow contamination problems (<4 m below ground surface) vapor extraction trenches combined with surface seals may be more effective than vertical wells. Trenches are usually limited to shallow soil zones because the difficulty of installation increases with depth.

Surface seals, such as polymer-based liners and asphalt, concrete, or clay caps, are sometimes used to control the vapor flow paths. Figure E-12 illustrates the effect that a surface seal will have on vapor flow patterns. For shallow treatment zones (<5 m) the surface seal will have a significant effect on the vapor flow paths, and seals can be added or removed to achieve the desired vapor flowpath. For wells screened below 8 m the influence of surface seals becomes less significant.

- *Well screening and construction*

Wells should be screened only through the zone of contamination, unless the permeability to vapor flow is so low that removal rates would be greater if flow were induced in an adjacent soil layer (see Figure E-6). Removal rate estimates for various mass-transfer limited scenarios can be calculated from Equations E-7 and E-12.

Based on Equation E-5, the flowrate is expected to increase by 15% when the extraction well diameter is increased from 10 cm (4 in) to 20 cm (8 in). This implies that well diameters should be as large as is practically possible.

A typical well as shown in Figure E-13a is constructed from slotted pipe (usually PVC). The slot size and number of slots per inch should be chosen to maximize the open area of the pipe. A filter packing, such as sand or gravel, is placed in the annulus between the borehole and pipe . Vapor extraction wells are similar to groundwater monitoring wells in construction but there is no need to filter vapors before they enter the well. The filter packing, therefore, should be as coarse as possible. Any dust carried by the vapor flow can be removed by an above-ground filter. Bentonite pellets and a cement grout are loaded above the filter packing. It is important that these be properly installed to prevent a vapor flow "short-sircuit". Any groundwater monitoring wells installed near the extraction wells must also be installed with good seals.

- *Vapor treatment*

Currently there are four main treatment processes available. Each is discussed below.

- *vapor combustion units:* Vapors are incinerated and destruction efficiencies are typically >95%. A supplemental fuel, such as propane, is added before combustion unless extraction well vapor concentrations are on the order of a few percent by volume. This process becomes less economical as vapor concentrations decrease below ≈10,000 ppm$_v$.

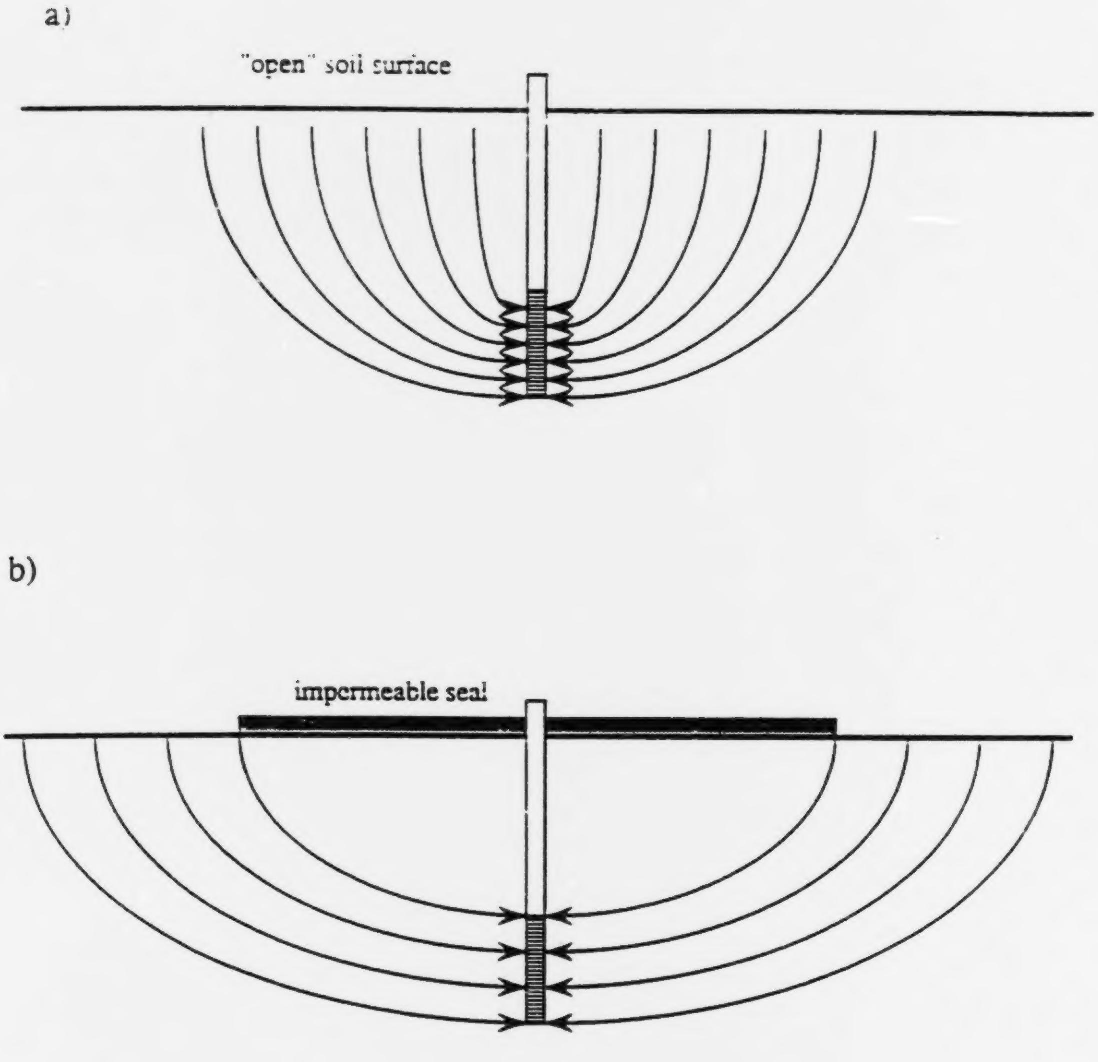

a)
"open" soil surface
b)
impermeable seal

Figure E-12. Effect of Surface Seal on Vapor Flowpath.

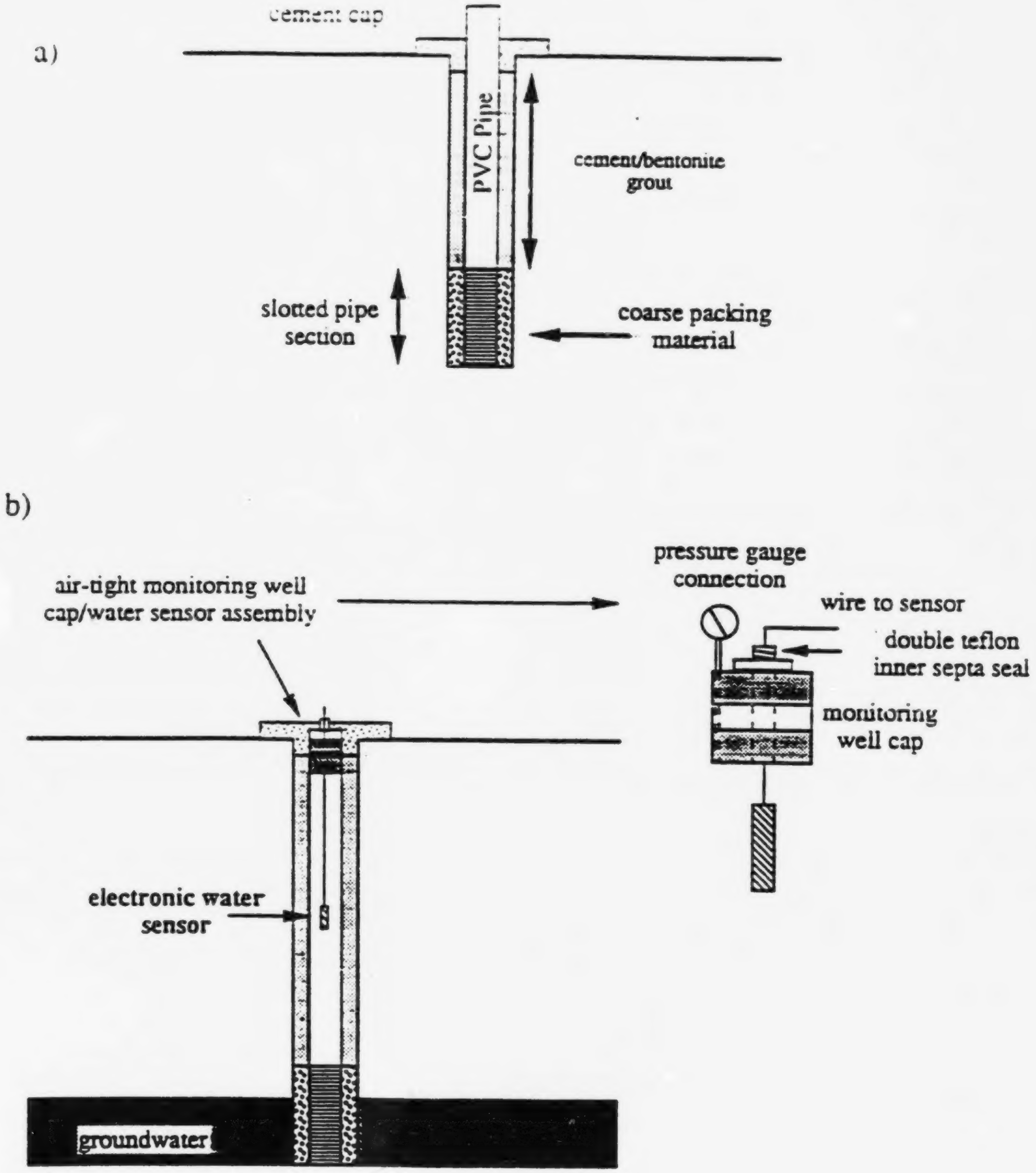

a)
cement cap
PVC Pipe
cement/bentonite grout
slotted pipe section
coarse packing material
b)
air-tight monitoring well cap/water sensor assembly
pressure gauge connection
wire to sensor
double teflon inner septa seal
monitoring well cap
electronic water sensor
groundwater

Figure E-13. a) Extraction Well Construction, and b) Air-Tight Groundwater Level Measuring System.

- *catalytic oxidation units*: Vapor streams are heated and then passed over a catalyst bed. Destruction efficiencies are typically >95%. These units are used for vapor concentrations <8000 ppm$_v$. More concentrated vapors can cause catalyst bed temperature excursions and melt-down.

- *carbon beds*: Carbon can be used to treat almost any vapor streams, but is only economical for very low emission rates (<100 g/d)

- *diffuser stacks*: These do not treat vapors, but are the most economical solution for areas in which they are permitted. They must be carefully designed to minimize health risks and maximize safety.

- *Groundwater pumping system*

In cases where contaminated soils lie just above or below the water table, groundwater pumping systems will be required to insure that contaminated soils remain exposed. In designing a groundwater system it is important to be aware that upwelling (draw-up) of the groundwater table will occur when a vacuum is applied at the extraction well (see Figure E-9b). Because the upwelling will be greatest at the extraction wells, groundwater pumping wells should be located within or as close to the extraction wells as possible. Their surface seals must be airtight to prevent unwanted short-circuiting of airflow down the groundwater wells.

- *System integration*

System components (pumps, wells, vapor treating units, etc.) should be combined to allow maximum flexibility of operation. The review by Hutzler et al.[1] provides descriptions of many reported systems. Specific requirements are:

- separate valves, flowmeters, and pressure gauges for each extraction and injection well.

- air filter to remove particulates from vapors upstream of pump and flow meter.

- knock-out pot to remove any liquid from vapor stream upstream of pump and flow meter.

Monitoring

The performance of a soil venting system must be monitored in order to insure efficient operation, and to help determine when to shut-off the system. At a minimum the following should be measured:

- ***date and time*** of measurement.

- ***vapor flow rates*** from extraction wells and into injection wells: these can be measured by a variety of flowmeters including pitot tubes, orifice plates, and rotameters. It is important to have calibrated these devices at the field operating pressures and temperatures.

- *pressure readings* at each extraction and injection well can be measured with manometers or magnahelic gauges.

- *vapor concentrations and compositions* from extraction wells: total hydrocarbon concentration can be measured by an on-line total hydrocarbon analyzer calibrated to a specific hydrocarbon. This information is combined with vapor flowrate data to calculate removal rates and the cumulative amount of contaminant removed. In addition, for mixtures the vapor composition should be periodically checked. It is impossible to assess if vapor concentration decreases with time are due to compositional changes or some other phenomena (mass transfer resistance, water table upwelling, pore blockage, etc.) without this information. Vapor samples can be collected in evacuated gas sampling cylinders, stored, and later analyzed.

- *temperature:* ambient and soil.

- *water table level* (for contaminated soils located near the water table): It is important to monitor the water table level to insure that contaminated soils remain exposed to vapor flow. Measuring the water table level during venting is not a trivial task because the monitoring well must remain sealed. Uncapping the well releases the vacuum and any effect that it has on the water table level. Figure E-13b illustrates a monitoring well cap (constructed by Applied Geosciences Inc., Tustin, CA) that allows one to measure simultaneously the water table level and vacuum in a monitoring well. It is constructed from a commercially available monitoring well cap and utilizes an electronic water level sensor.

Other valuable, but optional measurements are:

- *soil gas vapor concentrations and compositions:* these should be measured periodically at different radial distances from the extraction well. Figure E-14 shows the construction of a permanent monitoring installation that can be used for vapor sampling and subsurface temperature measurements. Another alternative for shallow contamination zones is the use of soil gas survey probes.

This data is valuable for two reasons: a) by comparing extraction well concentrations with soil gas concentrations it is possible to estimate the fraction of vapor that is flowing through the contaminated zone $f-C_{\text{extraction well}}/C_{\text{soil gas}}$, and b) it is possible to determine if the zone of contamination is shrinking towards the extraction well, as it should with time. Three measuring points are probably sufficient if one is located near the extraction well, one is placed near the original edge of the zone of contamination, and the third is placed somewhere in between.

These monitoring installations can also be useful for monitoring the subsurface vapors after venting has ceased.

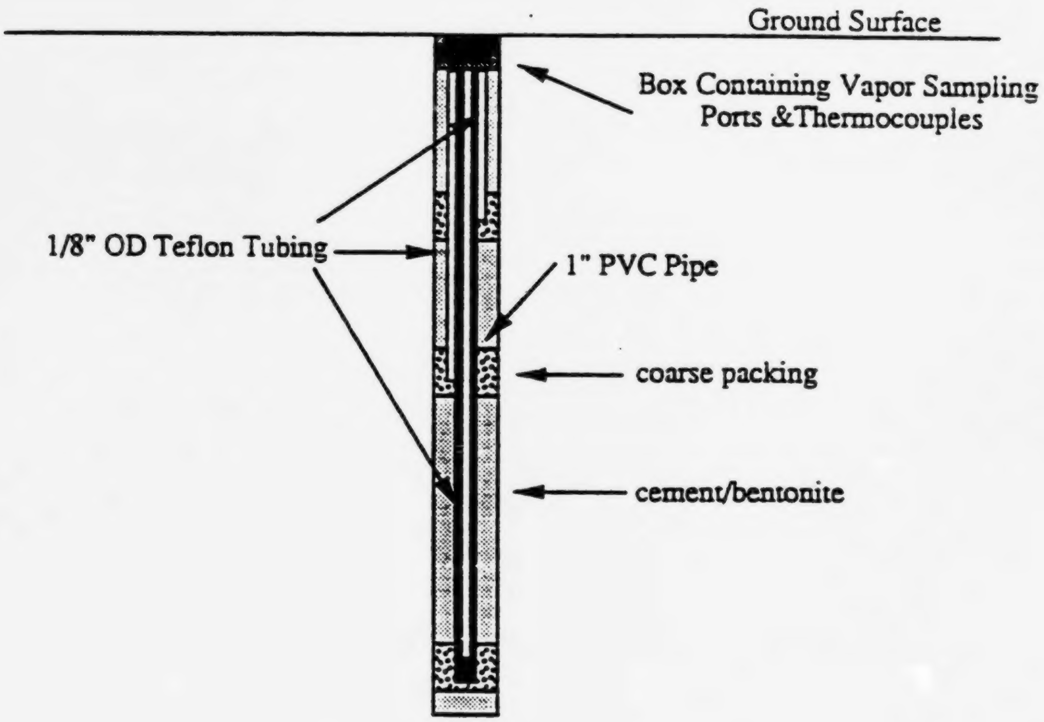

Ground Surface
Box Containing Vapor Sampling Ports &Thermocouples
1/8" OD Teflon Tubing
1" PVC Pipe
coarse packing
cement/bentonite

Figure E-14. Vadose Zone Monitoring Installation.

When To Turn Off The System?

Target soil clean-up levels are often set on a site-by-site basis, and are based on the estimated potential impact that any residual may have on air quality, groundwater quality, or other health standards. They may also be related to safety considerations (explosive limits). Generally, confirmation soil borings, and sometimes soil vapor surveys, are required before closure is granted. Because these analyses are expensive and often disrupt the normal business of a site, it would be valuable to be able to determine when confirmation borings should be taken. If the monitoring is done as suggested above, then the following criteria can be used:

- *cumulative amount removed*: determined by integrating the measured removal rates (flowrate x concentration) with time. While this value indicates how much contaminant has been removed, it is usually not very useful for determining when to take confirmation borings unless the original spill mass is known very accurately. In most cases that information is not available and can not be calculated accurately from soil boring data.

- *extraction well vapor concentrations*: the vapor concentrations are good indications of how effectively the venting system is working, but decreases in vapor extraction well concentrations are not strong evidence that soil concentrations have decreased. Decreases may also be due to other phenomena such as water table level increases, increased mass transfer resistance due to drying, or leaks in the extraction system.

- *extraction well vapor composition*: when combined with vapor concentrations this data gives more insight into the effectiveness of the system. If the total vapor concentration decreases without a change in composition, it is probably due to one of the phenomena mentioned above, and is not an indication that the residual contamination has been significantly reduced. If a decrease in vapor concentration is accompanied by a shift in composition towards less volatile compounds, on the other hand, it is most likely due to a change in the residual contaminant concentration. For residual gasoline clean-up, for example, one might operate a venting system until benzene, toluene, and xylenes were not detected in the vapors. The remaining residual would then be composed of larger molecules, and it can be argued that these do not pose a health threat through volatilization or leaching pathways.

- *soil gas contaminant concentration and composition*: this data is the most useful because it yields information about the residual composition and extent of contamination. Vapor concentrations can not be used to determine the residual level, except for very low residual levels (<500 mg/kg).

Other Factors

- *increased biodegradation*

It is often postulated that because the air supply to the vadose zone is increased, the natural aerobic microbiological activity is increased during venting. While the argument is plausible and some laboratory data is available[7], conclusive evidence supporting this theory has yet to be presented. This is due in part to the difficulty in making such a measurement. A mass balance approach is not likely to be useful because the initial spill mass is generally not known with sufficient accuracy. An indirect method would be to measure CO_2 levels in the extraction well vapors, but this in itself does not rule out the possibility that O_2 is converted to CO_2 before the vapors pass through the contaminated soil zone. The best approach is to measure the O_2/CO_2 concentrations in the vapors at the edge of the contaminated zone, and in the vapor extraction wells. If the CO_2/O_2 concentration ratio increases as the vapors pass through the contaminated soil, one can surmise that a transformation is occurring, although other possible mechanisms (inorganic reactions) must be considered. An increase in aerobic microbial populations would be additional supporting evidence.

- *in-situ heating/venting*

The main property of a compound that determines whether or not it can be removed by venting is its vapor pressure, which increases with increasing temperature. Compounds that are considered nonvolatile, therefore, can be removed by venting if the contaminated soil is heated to the proper temperature. In-situ heating/venting systems utilizing radio-frequency heating and conduction heating are currently under study[8]. An alternative is to reinject heated vapors from catalytic oxidation or combustion units into the contaminated soil zone.

- *air sparging*

Due to seasonal groundwater level fluctuations, contaminants sometimes become trapped below the water table. In some cases groundwater pumping can lower the water table enough to expose this zone, but in other cases this is not practical. One possible solution is to install air sparging wells and then inject air below the water table. Vapor extraction wells would then capture the vapors that bubbled up through the groundwater. To date, success of this approach has yet to be demonstrated. This could have a negative effect if foaming, formation plugging, or downward migration of the residual occurred.

Application of the Design Approach to a Service Station Remediation

In the following we will demonstrate the use of the approach discussed above and outlined in Figure E-2 for the design operation, and monitoring of an in-situ venting operation at a service station.

Preliminary Site Investigation

Prior to sampling it was estimated that 2000 gal of gasoline had leaked from a product line at this site. Several soil borings were drilled and the soil samples were analyzed for total petroleum hydrocarbons (TPH) and other specific compounds (benzene, toluene, xylenes) by a heated-headspace method utilizing a field GC-FID. Figure E-15 summarizes some of the results for one transect at this site. The following relevant information was collected:

- based on boring logs there are four distinct soil layers at this site between 0 - 18 m (0- 60 ft) below ground surface (BGS). Figure E-15 indicates the soil type and location of each of these layers.

- depth to groundwater was 15 m, with fine to medium sand aquifer soils

- the largest concentrations of hydrocarbons were detected in the sandy and silty clay layers adjacent to the water table. Some residual was detected below the water table. Based on the data presented in Figure E-15 it is estimated that ~ 4000 kg of hydrocarbons are present in the lower two soil zones.

- initially there was some free-liquid gasoline floating on the water table, and this was subsequently removed by pumping. A sample of this product was analyzed and its approximate composition (~20% of the compounds could not be identified) is listed in Table E-2 as the "weathered gasoline". The corresponding boiling point distribution curve for this mixture has been presented in Figure E-3.

- vadose zone monitoring installations similar to the one pictured in Figure E-14 were installed during the preliminary site investigation.

Deciding if Venting is Appropriate

For the remainder of the analysis we will focus on the contaminated soils located just above the water table.

- *What contaminant vapor concentrations are likely to be obtained?*

Based on the composition given in Table E-2, and using Equation E-1, the predicted saturated TPH vapor concentration for this gasoline is:

$$C_{sat} = 220 \text{ mg/l}$$

Using the "approximate" composition listed in Table E-2 yields a value of 270 mg/l. The measured soil vapor concentration obtained from the vadose zone monitoring well was 240 mg/l. Due to composition changes with time, this will be the maximum concentration obtained during venting.

- *Under ideal flow conditions is this concentration great enough to yield acceptable removal rates?*

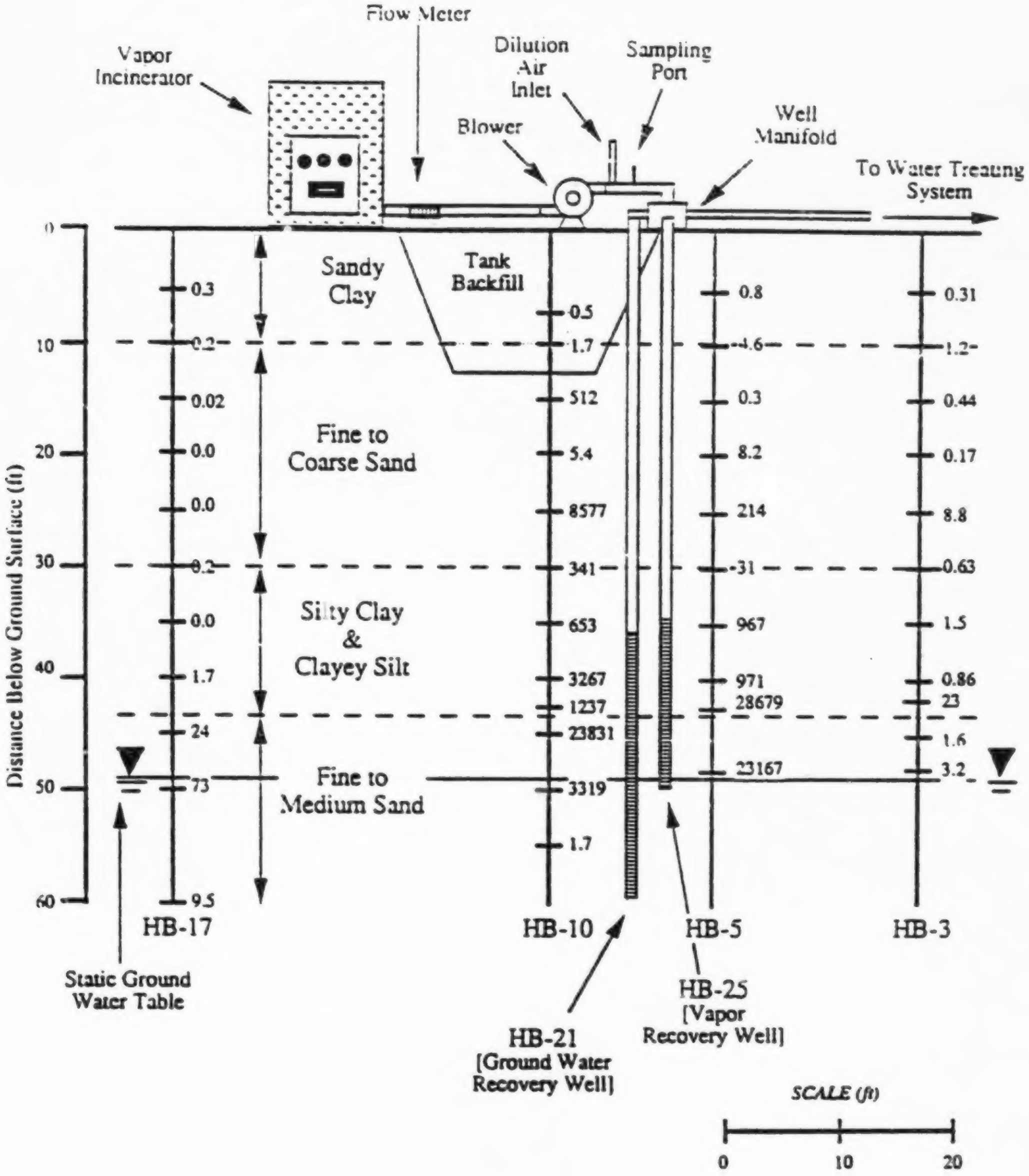

Flow Meter
Vapor Incinerator
Dilution Air Inlet
Sampling Port
Blower
Well Manifold
To Water Treating System
0
10
20
30
40
50
60
Distance Below Ground Surface (ft)
Sandy Clay
Tank Backfill
Fine to Coarse Sand
Silty Clay & Clayey Silt
Fine to Medium Sand
0.3
0.2
0.02
0.0
0.0
0.2
0.0
1.7
24
73
9.5
0.5
1.7
512
5.4
8577
341
653
3267
1237
23831
3319
1.7
0.8
4.6
0.3
8.2
214
31
967
971
28679
23167
0.31
1.2
0.44
0.17
8.8
0.63
1.5
0.86
23
1.6
3.2
HB-17
HB-10
HB-5
HB-3
Static Ground Water Table
HB-21 [Ground Water Recovery Well]
HB-25 [Vapor Recovery Well]
SCALE (ft)
0
10
20

Figure E-15. Initial Total Hydrocarbon Distribution [mg/kg-soil] and Location of Lower Zone Vent Well.

Equation E-4 was used to calculate $R_{acceptable}$. Assuming $M_{spill} = 4000$ kg and $t = 180$ d, then:

$$R_{acceptable} = 22 \text{ kg/d}$$

Using Equation E-2, $C_{est} = 240$ mg/l, and $Q = 2800$ l/min (100 cfm):

$$R_{est} = 970 \text{ kg/d}$$

which is greater than $R_{acceptable}$.

- What range of vapor flowrates can realistically be achieved?

Based on boring logs the contaminated zone just above the water table is composed of fine to medium sands, which have an estimated permeability $1 < k < 10$ darcy. Using Figure E-5, or Equation E-5, the predicted flowrates for an extraction well vacuum $P_w = 0.90$ atm are:

$0.04 < Q < 0.4$ m^3/m-min $R_w = 5.1$ cm, $R_I = 12$ m
$0.43 < Q < 4.3$ ft^3/ft-min $R_w = 2.0$ in, $R_I = 40$ ft

The thickness of this zone and probable screen thickness of an extraction well is about 2 m (6.6 ft). The total flowrate per well through this zone is estimated to be $0.08<Q<0.8$ m^3/min (2.8 cfm<Q<28 cfm).

- Will the contaminant concentrations and estimated flowrates produce acceptable removal rates?

Using $C_{est}=240$ mg/l, the maximum removal rates likely to be obtained are calculated from Equation E-2:

$$28 \text{ kg/d} < (R_{est})_{max} < 280 \text{ kg/d}$$

To be conservative, we will guess that only 50% of the vapor actually flows through contaminated soils, so our estimated removal rate per well will be half of these values. The estimated acceptable removal rate $R_{acceptable} = 22$ kg/d falls within this range. Of course this calculation did not take into account the possibility of vapor concentration decreases during venting. We shall take this into account in the next subsection.

- What residual, if any, will be left in the soil?

A target clean-up level for most gasoline spill sites is <1000 mg/kg TPH residual. If our initial residual level is ~10,000 ppm, then we need to remove at least 90% of the initial residual. According to the curves in Figure E-9, which represent the maximum removal rates for the gasoline analyzed at this site, approximately 100 l-vapor/g-residual will have to pass through the contaminated zone to achieve this target. Based on our estimated initial residual of 4000 kg TPH, 4×10^8 l-vapor are required. Over a six month period this corresponds to an average flowrate $Q=1.5\ m^3/min$ (54 cfm). Recall that since this corresponds to the maximum removal rate, it is the minimum required flowrate.

- *Are there likely to be any negative effects of soil venting?*

Given that the contaminated soils are located just above and below the water table, water table upwelling during venting must be considered here.

Air Permeability Test

Figure E-16 presents data obtained from the air permeability test of this soil zone. In addition to vapor extraction tests, air injection tests were conducted. The data is analyzed in the same manner as discussed for vapor extraction tests. Accurate flowrate (Q) values were not measured, therefore, Equation E-17 was used to determine the permeability to vapor flow. The k values ranged from 2 to 280 darcys, with the median being ~8 darcys.

System Design

- *Number of vapor extraction wells:*

Based on the 8 darcys permeability, and assuming a 15 cm diameter (6 in) venting well, a 2 m screened section, $P_w = 0.90$ atm (41 in H_2O vacuum) and $R_I=12$ m, then Equation E-5 predicts:

$$Q = 0.7\ m^3/min = 25\ cfm$$

Based on the discussion above, a minimum average flowrate of 1.5 m^3/min is needed to reduce the residual to 1000 ppm in 6 months. The number of wells required is then $1.5/0.7 = 2$, assuming that 100% of the vapor flows through contaminated soils. It is not likely that this will occur, and a more conservative estimate of 50% vapor flowing through contaminated soils would require that twice as many wells (4) be installed.

A single vapor extraction well (HB-25) was installed in this soil layer with the knowledge that more wells were likely to be required. Its location and screened interval are shown in Figure E-15. Other wells were installed in the clay layer and upper sandy zone, but in this paper we will only discuss results from treatment of the lower contaminated zone. A groundwater pumping well was installed to maintain a 2 m drawdown below the static water level. Its location is also shown in Figure E-15.

System Monitoring

Three vadose monitoring wells similar in construction to the one pictured in Figure E-14 were installed so that the soil temperature, soil gas

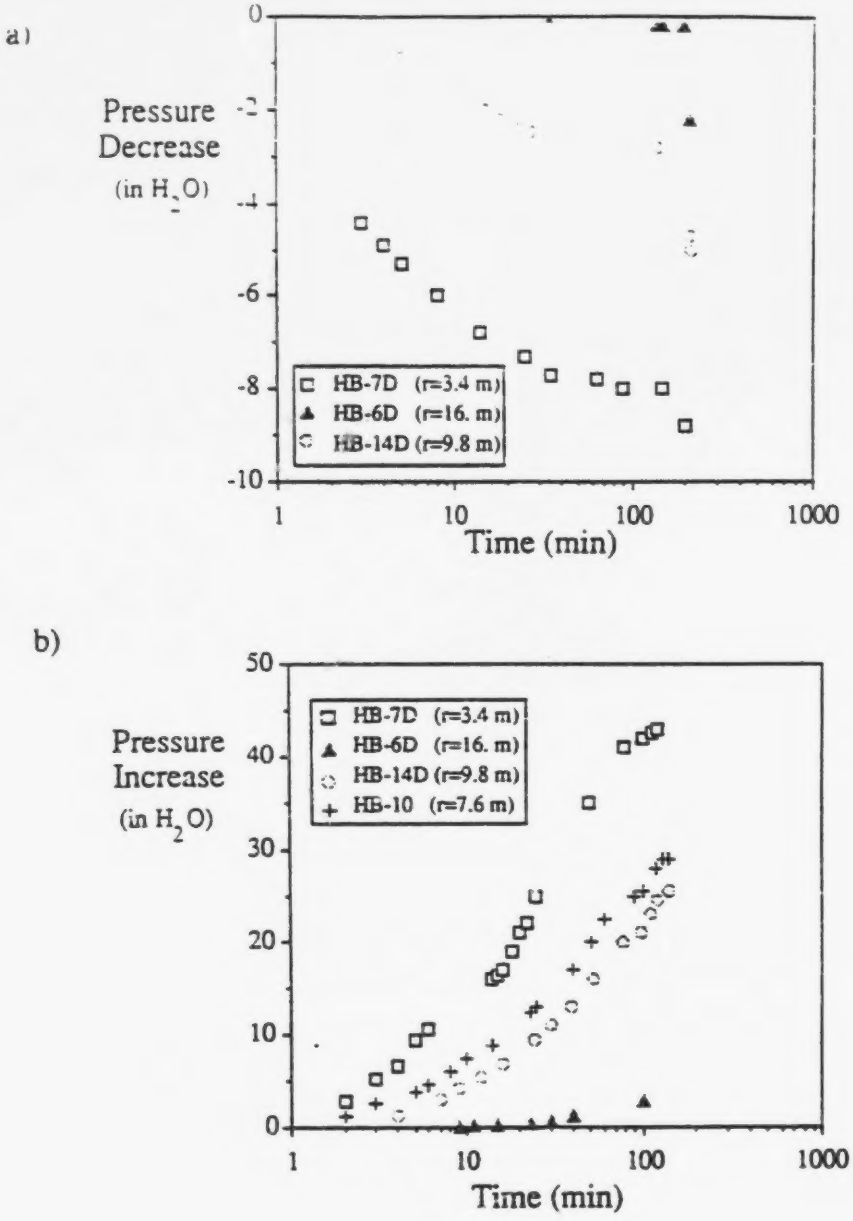


Figure E-16. Air Permeability Test Results: a) vapor extraction test, b) air injection test.

concentrations, and subsurface pressure distribution could be monitored at three depths. One sampling port is located in the zone adjacent to the aquifer. The vapor flowrate from HB-25 and vapor concentrations were measured frequently, and the vapor composition was determined by GC-FID analysis. In addition, the water level in the groundwater monitoring wells was measured with the system pictured in Figure E-13b. The results from the first four months of operation are discussed below.

In Figure E-17a the extraction well vacuum and corresponding vapor flowrate are presented. The vacuum was maintained at 0.95 atm (20 in H_2O vacuum), and the flowrate was initially 12 scfm. It gradually decreased to about 6 scfm over 80 d. For comparison, Equation (5) predicts that Q=12 cfm for k=8 darcys. Increasing the applied vacuum to 0.70 atm (120 in H_2O vacuum) had little effect on the flowrate. This could be explained by increased water table upwelling, which would act to decrease the vertical cross-section available for vapor flow. The scatter in the flowrate measurements is probably due to inconsistent operation of the groundwater pumping operation, which frequently failed to perform properly.

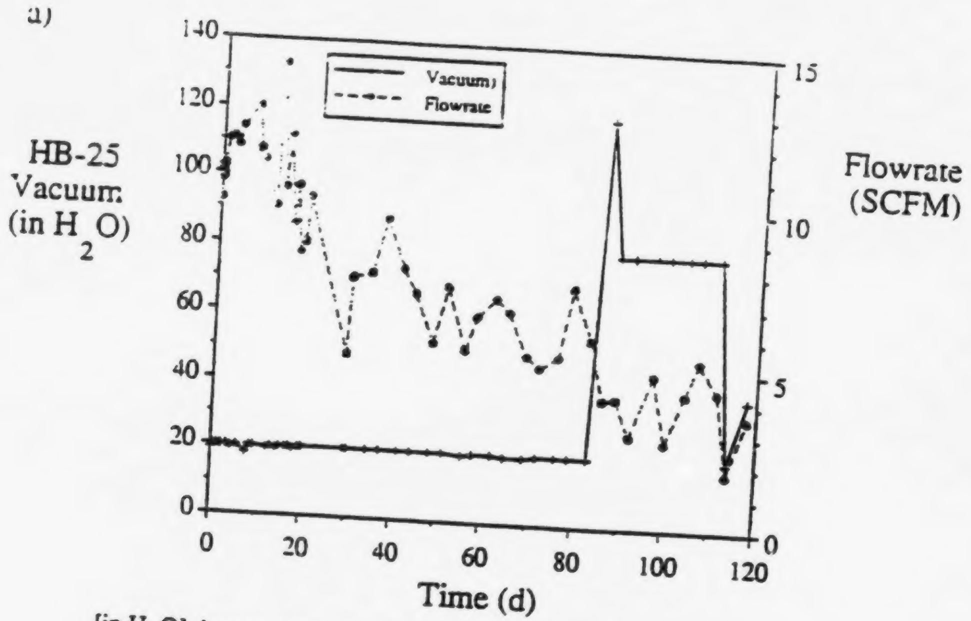
Figure E-17b presents the change in vapor concentration with time. Fifteen specific compounds were identified during the GC-FID vapor analyses; in this figure we present the total concentration of known and unknown compounds detected between five boiling point ranges:

methane - isopentane (<28°C)
isopentane - benzene (28 - 80°C)
benzene - toluene (80 - 111°C)
toluene - xylenes (111 - 144°C)
>xylenes (>144°C)

There was a shift in composition towards less volatile compounds in the first 20 d, but after that period the composition remained relatively constant. Note that there is still a significant fraction of volatile compounds present. Within the first two days the vapor concentration decreased by 50%, which corresponds to the time period for the removal of the first pore volume of air. Comparing the subsequent vapor concentrations with the concentrations measured in the vadose zone monitoring wells indicates that only (80 mg/l)/(240 mg/l)*100=33% of the vapors are flowing through contaminated soil.

Figure E-18a presents calculated removal rates (flowrate x concentration) and cumulative amount (1 gal = 3 kg) removed during the first four months. The decrease in removal rate with time is due to a combination of decreases in flowrate and hydrocarbon vapor concentrations. After the first four months approximately one-fourth of the estimated residual has been removed from this lower zone.

On day 80 the vacuum was increased from 20 - 120 in H_2O vacuum and the subsequent increase in subsurface vacuum and water table upwelling was monitored. Figure E-18b presents the results. Note that the water table rise paralleled the vacuum increase, although the water table did not rise the same amount that the



[in H_2O] denote vacuums expressed as equivalent water column heights

Figure E-17a. Soil Venting Results: Vacuum/Flowrate Data

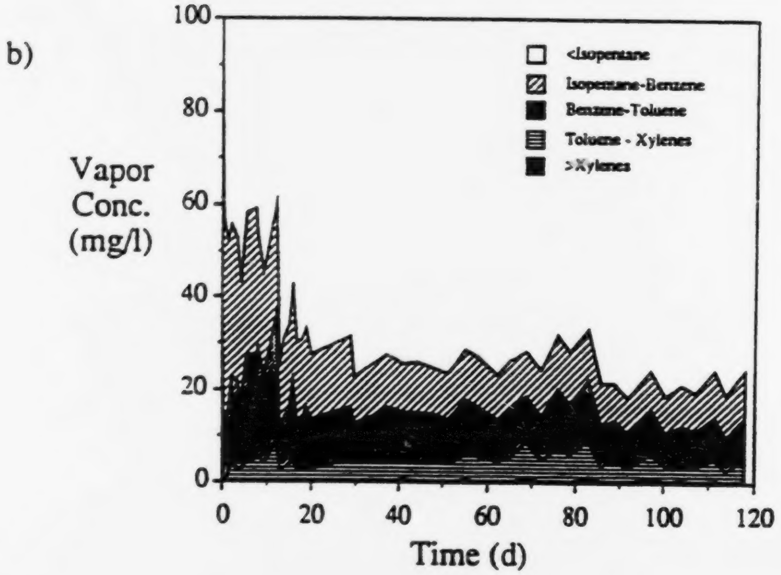
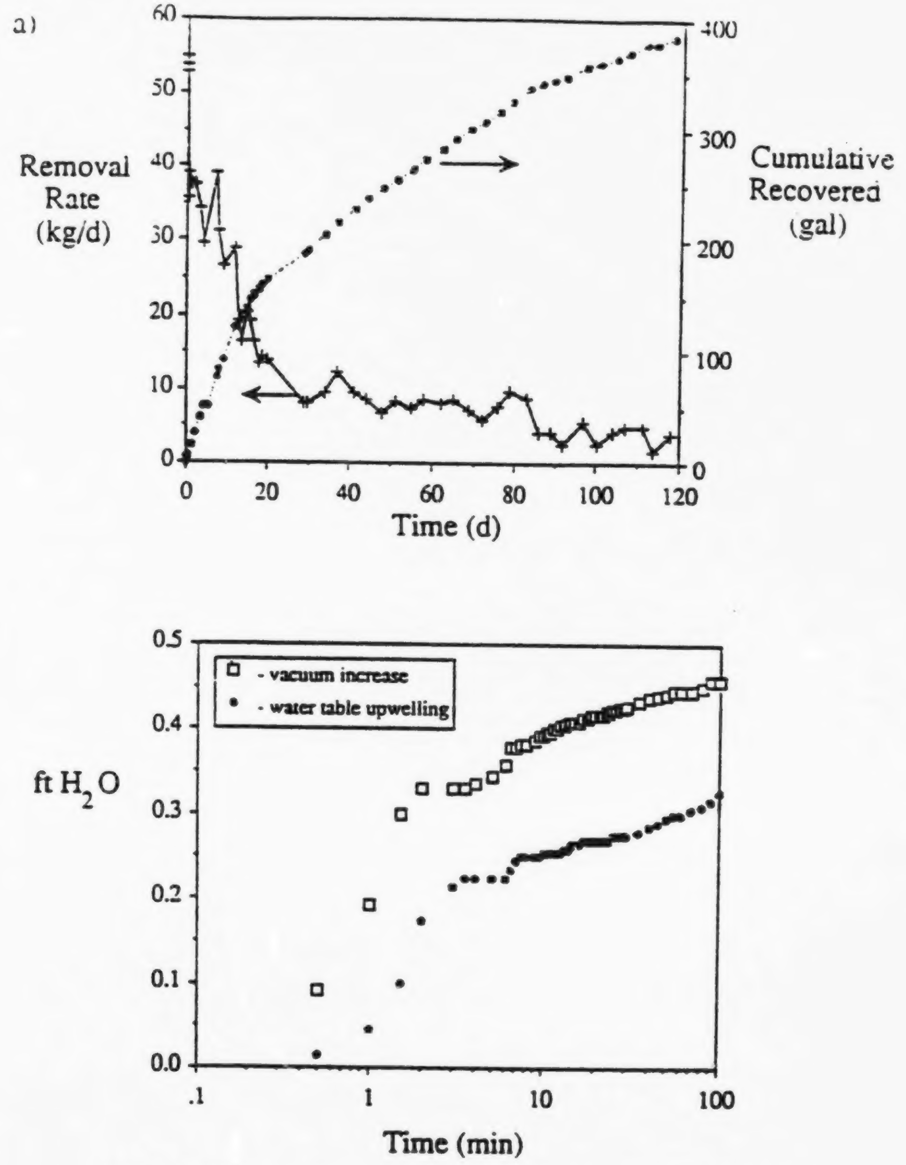


Figure E-17b. Soil Venting Results: Concentration/Composition Data



[ft H_2O] denote vacuums expressed as equivalent water column heights

Figure E-18. Soil Venting Results: a) Removal Rate/Cumulative Recovered, b) Water Table Rise.

vacuum did.

Figure E-19 compares the reduced measured TPH vapor concentration C(t)/C(t=0) with model predictions. C(t=0) was taken to be the vapor concentration after one pore volume of air had passed through the contaminated zone (≈80 mg/l), m(t=0) is equal to the estimated spill mass (≈4000 kg), and V(t) is the total volume of air that has passed through the contaminated zone. This quantity is obtained by integrating the total vapor flowrate with time, then multiplying it by the fraction of vapors passing through the contaminated zone f (≈0.33). As discussed, the quantity f was estimated by comparing soil gas concentrations from the vadose zone monitoring installations with vapor concentrations in the extraction well vapors. As can be seen, there is good quantitative agreement between the measured and predicted values.

Based on the data presented in Figures E-15 through E-19 and the model predictions in Figure E-8, it appears that more extraction wells (~10 more) are needed to remediate the site within a reasonable amount of time.

CONCLUSIONS

A structured, technically based approach has been presented for the design, construction, and operation of venting systems. While we have attempted to explain the process in detail for those not familiar with venting operations or the underlying governing phenomena, the most effective and efficient systems can only be designed and operated by personnel with a good understanding of the fundamental processes involved. The service station spill example presented supports the validity and usefulness of this approach.

There are still many technical issues that need to be resolved in the future. In particular, we must be able to estimate removal rates for non-ideal situations, demonstrate that biodegradation is enhanced by venting, and investigate novel ideas for enhancing venting removal rates.

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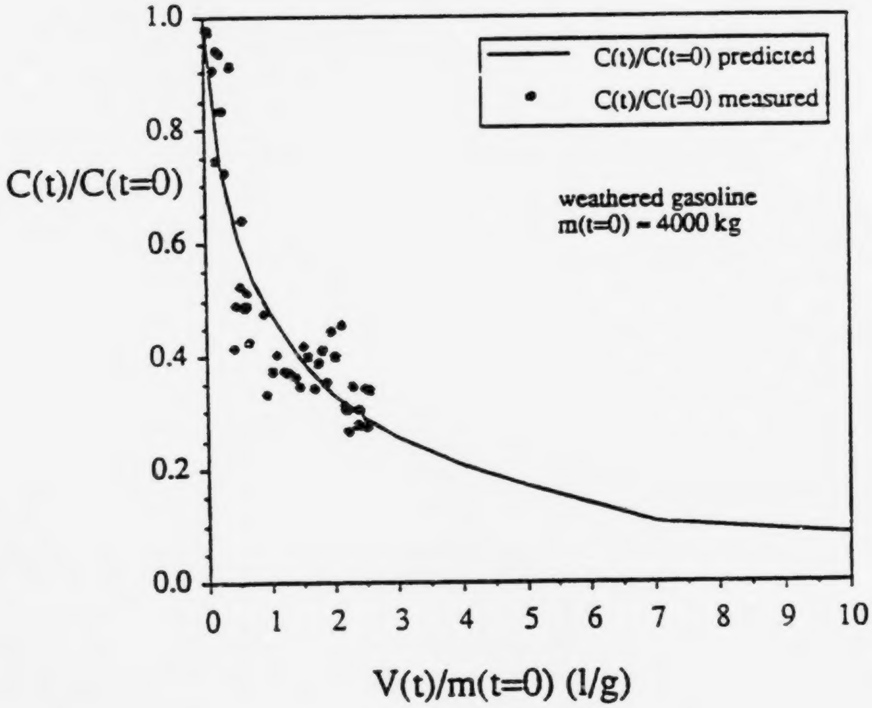

Figure E-19. Comparison of Model Predictions and Measured Response.

APPENDIX F - ARTICLE ON INCINERATION
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INCINERATION OF HAZARDOUS WASTE
A Critical Review

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Over the last ten years, concern over improper disposal practices of the past has manifested itself in the passage of a series of federal and state-level hazardous waste clean-up and control statutes of unprecedented scope. The impact of these various statutes will be a significant modification of waste management practices. The more traditional and lowest cost methods of direct landfilling, storage in surface impoundments and deep-well injection will be replaced, in large measure, by waste minimization at the source of generation, waste reuse, physical/chemical/biological treatment, incineration and chemical stabilization/solidification methods. Of all of the "terminal" treatment technologies, properly-designed incineration systems are capable of the highest overall degree of destruction and control for the broadest range of hazardous waste streams. Substantial design and operational experience exists and a wide variety of commercial systems are available. Consequently, significant growth is anticipated in the use of incineration and other thermal destruction methods. The objective of this review is to examine the current state of knowledge regarding hazardous waste incineration in an effort to put these technological and environmental issues into perspective.

Hazardous waste management is the environmental issue of the 1980s. Discovery of the numerous environmental catastrophes resulting from the improper disposal practices of the past have elevated public awareness and concern. Over the last ten years, this concern has manifested itself in the passage of a series of federal and state-level hazardous waste clean-up and control statutes of unprecedented scope and impact. At the federal level these laws include the Resource Conservation and Recovery Act of 1976 (RCRA) and its "cradle to grave" provisons for controlling the storage, transport, treatment, and disposal of hazardous waste. In 1979, the PCB regulations promulgated under Section 6(e) of the Toxic Substances Control Act (TSCA), prohibited the further manufacture of polychlorinated biphenyls (PCBs) after July 2, 1979, established limits on PCB use in commerce, and established regulations for proper disposal. Clean-up of the uncontrolled waste sites created by poor disposal practices of the past was provided for in the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) which established a national fund (Superfund) to assist in remedial actions. The 1986 Superfund Amendments and Reauthorization Act (SARA) not only reauthorized the Superfund program but greatly expanded the provisions and funding of the initial Act.

The most significant of all of these statutes were the 1984 amendments and reauthorization of RCRA. Termed the Hazardous and Solid Waste Act of 1984 (HSWA), these amendments establish a strict timeline for restricting untreated hazardous waste from land disposal. By 1990, most wastes will be restricted and pretreatment standards will be established based upon the treatment levels achievable by Best Demonstrated Available Technology (BDAT).[1]

The impact of these various statutes will be a significant modification of waste management practices. The more traditional and lowest cost methods of direct landfilling, storage in surface impoundments and deep-well injection will be replaced, in large measure, by waste minimization at the source of generation, waste reuse, physical/chemical/biological treatment, incineration and chemical stabilization/solidification methods.

Of all of the "terminal" treatment technologies, properly-designed incineration systems are capable of the highest overall degree of destruction and control for the broadest range of hazardous waste streams. Substantial design and operational experience exists and a wide variety of commercial systems are available. Consequently, significant growth is anticipated in the use of incineration and other thermal destruction methods.[2]

While thermal destruction offers many advantages over existing hazardous waste disposal practices and may help to

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meet the anticipated need for increased waste management capacity, public opposition to the permitting of new thermal destruction operations has been strong in recent years.[3] The environmental awareness and activism which spawned the major hazardous waste laws of the 1980s have in many respects switched to skepticism over the safety and effectiveness of the technological solutions which the laws were designed to implement. Citizen distrust of the waste management facility owners and operators remains. The ability of government agencies to enforce compliance is questioned. Reports of trace quantities of chlorinated dioxins, chlorinated furans, and other combustion byproducts in the stack emissions of municipal solid waste and PCB incinerators have raised questions in the minds of some concerning whether the RCRA incinerator standards are sufficient to protect public health and the environment. Yet, waste generators, faced with the specter of complying with the HSWA land disposal restrictions or faced with the prospect of future multimillion dollar environmental damage settlements over contaminated groundwater, are looking to ultimate destruction techniques such as incineration as their only viable alternative.

The objective of this review is to examine the current state of knowledge regarding hazardous waste incineration in an effort to put these technological and environmental issues into perspective. In doing so, it will be important to review:

- Current and emerging regulations and standards for hazardous waste incinerators;
- Current incineration technology and practice;
- Capabilities and limitations of methods for measuring process performance;
- Destruction efficiency and emissions characterization of current technology;
- Methods for predicting and assuring incinerator performance;
- Environmental and public health implications of hazardous waste incineration; and
- Remaining issues and research needs.

While the focus of the paper is on hazardous waste incineration, it is important to understand that many of the same issues relate to municipal waste incineration and to the use of hazardous waste as a fuel in industrial boilers and furnaces. Where possible and appropriate the performance and emissions of these systems will be compared and contrasted with hazardous waste incinerators.

Background

Historical Perspective

Purification by fire is an ancient concept. Its applications are noted in the earliest chapters of recorded history. The Hebrew word for hell, *Gehenna*, was actually derived from the ancient phrase *ge-ben Hinnom* or the valley of the son of Hinnom, an area outside of Jerusalem which housed the smoldering town dump and was the site of propitiatory sacrifices to Moloch II.[4] Today, waste fires on the ground or in pits are still used by nomadic tribes.

In the Middle Ages an early innovation to waste fires was the "fire wagon," the first mobile incinerator.[5] It was a simple rectangular wooden wagon protected by a clay lining. The horse-drawn wagon traveled the streets allowing residents to throw their refuse into the moving bonfire.

Incineration as we know it today began slightly more than one hundred years ago when the first municipal waste "destructor" was installed in Nottingham, England.[5] Incineration use in the United States grew rapidly also, from the first installation on Governor's Island in New York to more than 200 units in 1921. Most of these were poorly operated batch feed units, some with steam recovery. Until the 1950s, incinerators and their attendant smoke and odors were considered a necessary evil and their operations were generally undertaken in the cheapest possible manner. However, as billowing smoke stacks became less of a symbol of prosperity and air pollution regulations began to emerge, incineration systems improved dramatically.[6] These improvements included continuous feed, improved combustion control, the use of multiple combustion chambers, designs for energy recovery and the application of air pollution control systems.[7]

Incineration has been employed for disposal of industrial chemical wastes (hazardous waste) for slightly more than 20 years. Initial units borrowed on municipal waste technology, but poor performance and adaptability of these early grate-type units lead to the subsequent use of rotary kilns. Many of the earliest rotary kiln facilities were in West Germany. One of the first United States kiln units was at the Dow Chemical Company facility in Midland, Michigan.

Regulations

The first U.S. federal standards for control of incineration emissions were applied to municipal waste combustors under the New Source Performance Standards (NSPS) provisions of the Clean Air Act of 1970. The NSPS established a time-averaged (2 hours) particulate emission limit of 0.08 grains per dry standard cubic foot (gr/dscf), corrected to 12 percent CO_2, for all incineration units constructed after August 1971 and having charging rates greater than 50 tons per day (tpd). Opacity limits were not promulgated at the federal level, but many states now have their own opacity limits and, in some cases, more stringent particulate control requirements.

Hazardous waste incinerators were not regulated until the passage of the Resource Conservation and Recovery Act of 1976 (RCRA). Technical standards for incinerators were proposed in December 1978 under Section 3004 of RCRA.[8] These standards provided both performance and operating

Table I. Quantities of incinerable wastes generated in the United States, 1983.[27]

Type of waste	Quantity generated (MMT)[a]	Current percent recycled/ recovered[b]	Quantity after recycled/ recovered[b] (MMT)
Liquids:			
Waste oils	14.25	11	12.68
Halogenated solvents	3.48	70	1.04
Nonhalogenated solvents	12.13	70	3.64
Other organic liquids	3.44	2	3.37
Pesticides/herbicides	0.026	55	0.012
PCBs	0.001	0	0.001
Total liquids	33.33	38	20.74
Sludge and Solids:			
Halogenated sludges	0.72	0	0.72
Nonhalogenated sludges	2.24	0	2.24
Dye and paint sludges	4.24	0	4.24
Oily sludges	3.73	5	3.54
Halogenated solids	9.78	0	9.78
Nonhalogenated solids	4.58	0	4.58
Resins, latex, monomer	4.02	65	1.41
Total sludges/solids	29.31	10	26.51
Total incinerable wastes	62.64	25	47.25
Total hazardous wastes	265.60	6	249.28

[a] MMT = millions of metric tons.

[b] These waste recycling and recovery practice estimates were derived by the Congressional Budget Office from information obtained directly through surveys of industrial waste generators and the waste recovery industry.[25]

requirements. The performance standards included requirements for acceptable levels of combustion efficiency, destruction efficiency, halogen removal efficiency, and an emission limit for particulate matter. Operational standards required semicontinuous monitoring of process variables (e.g., CO) and specific minimum temperature and combustion gas residence time levels. During the allowable comment period on the proposed rules, EPA received extensive comment on the scope of the standards and the adequacy of the combined EPA and industrial data base used to set the standards.

Based upon the public comment, EPA subsequently proceeded down a three-phase regulatory path:

- Phase I (May 19, 1980). Interim status standards were proposed outlining operating procedures to be followed by existing incinerator facilities.[9]
- Phase II (January 23, 1981). Performance standards were proposed for new incineration facilities, requiring specific levels of organic hazardous constituent destruction and removal, exhaust gas HCl removal, and maximum particulate emission concentration.[10]
- Phase III (June 24, 1982). Interim final standards were published for both new and existing incinerators, incorporating and modifying somewhat the provisions of the Phase I and Phase II rules.[11]

The provisions of the final incinerator standards, which are of most importance to this paper, are the performance standards which are now listed in the Code of Federal Regulations (CFR) under 40 CFR 264.343. These standards require that in order for a facility to receive a RCRA permit, it must attain the following performance levels:

(1) 99.99 percent destruction and removal efficiency (DRE) for each principal organic hazardous constituent (POHC) in the waste feed where:

$$\mathrm{DRE} = [(W_{in} - W_{out})/W_{in}] \times 100$$

where: W_{in} = mass feed rate of the principal organic hazardous constituent (POHC) in the waste stream fed to the incinerator, and

W_{out} = mass emission rate of the POHC in the stack prior to release to the atmosphere.

(2) At least 99 percent removal of hydrogen chloride from the exhaust gas if hydrogen chloride stack emissions are greater than 1.8 kg/h.

(3) Particulate matter emissions no greater than 180 mg/standard m^3 corrected to 7 percent oxygen in the stack gas. The measured particulate matter concentration is multiplied by the following correction factor to obtain the corrected particulate matter emissions:

$$\text{Correction factor} = 14/(21 - Y)$$

where: Y = measured oxygen concentration in the stack gas on a dry basis (expressed as a percentage).

The concept and selection of POHCs is an important part of the incineration regulations. POHCs, which are to be sampled during "trial burns" to assess attainment of the standards, are to be selected from the RCRA Appendix VIII constituents present in the wastes.[10] Appendix VIII is a list of approximately 400 organic and inorganic hazardous chemicals first published in Part 261 of the May 19, 1980 *Federal Register*.[9] The list is updated semiannually in 40 CFR 261.

POHC selection guidance suggests that Appendix VIII constituents which are in the highest concentration in the waste feed and are the most difficult to incinerate are the most likely and appropriate to be selected as POHCs.[12] This selection approach, particularly the concept of hazardous compound incinerability, has been the subject of considerable scientific debate since the guidance was first proposed in 1981. These issues will be examined in greater detail later.

It is important to note that EPA chose not to apply the incineration standards to the practice of disposing of hazardous waste as a fuel in industrial boilers and furnaces.[9] This exemption was based upon a lack of sufficient information on the practice and the fact that energy recovery constituted a beneficial use of wastes. Considerable data have been assembled since the exemption was granted in 1980. EPA began to control the practice first in 1985 with issuance of RCRA regulations on the use of waste oil for energy recovery.[13] This rule provides a basis for distinguishing between a used oil and a hazardous waste for energy recovery purposes and provides a used oil specification that limits the types of boilers that can burn used oils that fail the specification. EPA is developing regulations which will cover the disposal of hazardous waste in industrial boilers and other industrial process furnaces. These rules are currently scheduled for proposal in 1987.[14]

EPA has also promulgated regulations for the incineration of specific wastes. Incineration of PCBs (polychlorinated biphenyls) is controlled under TSCA rules promulgated in May 1979.[15] These rules require that whenever disposal of PCBs is undertaken, they must be incinerated, unless the PCB concentration is less than 50 parts per million (ppm). If the concentration is between 50 and 500 ppm, the rule provides for certain exceptions that allow alternatives to the incineration requirements, such as use as fuel in high efficiency boilers. Where the concentration exceeds 500 ppm, PCBs must be disposed of in incinerators which achieve a 99.9 percent combustion efficiency (CE), and meet a number of specific incinerator operating conditions (combustion temperature, residence time, stack oxygen concentration).

The incineration of certain wastes containing certain chlorinated dibenzo-*p*-dioxins, chlorinated dibenzofurans, and chlorinated phenols is regulated under RCRA rules promulgated January 14, 1985. The so-called "dioxin rule" limits the incineration of these specific wastes (EPA waste codes F020-F028) to incinerators which have been "certified" as being capable of achieving 99.9999 percent DRE for chlorinated dioxins or similar compounds.[16]

Current municipal waste incineration standards under the Clean Air Act provide only limits on particulate emissions, as previously stated. The 1984 Hazardous and Solid Waste Act Amendments (Section 102), however, require EPA to prepare a Report to Congress on the extent of risks due to dioxin emissions from municipal waste incinerators and on appropriate methods for reducing these emissions. EPA also plans to expand the report to include data on cancer risks and controls associated with additional pollutants emitted by these incinerators. EPA is committed by an agreement with the Natural Resources Defense Council to issue an announcement by May 1987 on what actions EPA plans to take regarding risks from municipal waste incineration.

Current Incineration Practice

Incineration Practice

Incineration is an engineered process that employs thermal decomposition via thermal oxidation at high temperature (usually 900°C or greater) to destroy the organic fraction of the waste and reduce volume. Generally, combustible wastes or wastes with significant organic content are considered most appropriate for incineration. However, technically speaking, any waste with a hazardous organic fraction, no matter how small, is at least a functional candidate for incineration. For instance, significant amounts of contaminated water are currently incinerated in the United States.[17] Contaminated soils are also being incinerated with increasing frequency. EPA, for example, has employed a mobile incinerator to decontaminate 40 tons of Missouri soil which had been contaminated with four pounds of chlorinated dioxin compounds.[18] Many other designs for mobile incineration facilities have emerged and are also being applied in the field for decontamination of soil and debris.[19]

Since the promulgation of the RCRA interim status incinerator standards in 1980, a number of surveys and studies have been conducted to assess the quantity and types of hazardous waste generated in the United States as well as the quantities and types of wastes being managed by various treatment storage and disposal facilities.[20–26] These studies often reveal significant differences in what would seem to be relatively straightforward statistics. While frustrating to those in government and industry who are evaluating waste management alternatives and economic impacts, these deficiencies in the data base are not surprising. They have resulted from many factors: changes and uncertainties in regulatory definitions of hazardous waste terms; differences in methods and assumptions employed in the various surveys; and incomplete or inaccurate responses by facility owners and operators. Continuing changes in waste generation and the number and permit status of facilities which have occurred in response to regulatory changes and economic factors have also made it difficult to accurately project waste management practice from one point in time to another.

In spite of these deficiencies and limitations, it is possible to construct a reasonable picture of hazardous waste generation and incineration practice from the aggregate of the studies. Total annual hazardous waste generation in the United States appears to be approximately 265 million metric tons (MMT). This number was first projected by EPA in the so-called Westat mail survey[24] and later confirmed in separate studies by the Congressional Budget Office (CBO),[25] and the Congressional Office of Technology Assessment (OTA).[26] Only a small fraction of this waste (<1 percent) was believed to have been incinerated. EPA estimated that 1.7 MMT was disposed in incinerators in 1981[24] and CBO projected this amount at 2.7 MMT in 1983.[25]

Precise infromation on the exact types of wastes actually going to incineration facilities is not available. Many facilities operate on an intermittent basis and handle mixtures of wastes which are difficult to describe in terms of EPA standard waste codes. A 1983 EPA study examined data on 413 waste streams going to 204 incineration facilities in the United States.[17] The major waste streams incinerated were spent nonhalogenated solvents (EPA waste code F003) and corrosive and reactive wastes contaminated with organics (EPA waste codes D002 and D003). Together, these accounted for 44 percent of the waste incinerated. Other prominent wastes included hydrocyanic acid (P063), acrylonitrile bottoms (K011), and nonlisted ignitable wastes (D001).

While only a small fraction of available hazardous waste is currently managed by incineration, many believe that implementation of the HSWA land disposal restriction regulations and generator concern for long-term liability will result in increased utilization of incineration for ultimate disposal. EPA has estimated that nearly five times more hazardous waste could have been thermally destroyed in incinerators and industrial furnaces in 1981 than actually was.[24] Numerous other studies have indicated that the actual use and demand for incineration technologies to manage hazardous waste will increase significantly.[2,25,27–29]

The CBO study, however, offers the best perspective of potential hazardous waste incineration practice.[25] These data, which are based upon industrial output models, are the only available source of comprehensive waste generation estimates which are aggregated on the basis of waste type. This allows more precise estimation of incinerable waste quantities. CBO also examined the potential impact of waste reduction and recycling activities on waste available for incineration. The results of these analyses (Table I) indicated that even after recycling and reduction, as much as 47 MMT per year could have been available for incineration in 1983. This estimate, however, did not include potentially incinerable wastes from uncontrolled hazardous waste sites.

It is clear that considerable potential exists for expansion of incineration practice. This assumes, however, sufficient RCRA-permitted capacity can be made available. This is, of course, a significant issue and one which has been given attention in a number of studies.[2,20–23] While capacity appears to be adequate in the near term, (Table II) waste quantities received for incineration appear to be increasing at a faster rate than capacity is being added.[20] Beyond this, future increases in demand will be primarily for organic solids and sludges (e.g., wastes restricted from land disposal or resulting from uncontrolled site clean-up). Liquid capacity will likely remain sufficient for a longer time, especially if the capacity represented by potential disposal in cement kilns and industrial boilers is included.[2]

One of the major barriers to increased incineration capacity is public opposition to the permitting and siting of new facilities, especially the off-site commercial facilities which would be necessary to handle much of the solids and sludges which will increasingly require suitable disposal. Public opposition to the permitting of new thermal destruction operations has been strong in recent years. The normal time required for permitting new incineration facilities is three years. This time, as well as the expense of obtaining a permit,

Table II. Estimation of available hazardous waste incinerator capacity by incinerator design.[22]

Incinerator design	Number of units Reported	Projected[e]	Reported average design capacity[a] (MM Btu/h)	Reported utilization[b] (percent)	Projected available capacity[c] (MM Btu/h)	Percent with air pollution control equipment
Rotary kiln	42	45	61.37	77	635	90
Liquid injection	95	101	28.26	55	1284	42
Fume	25	26	33.14	94	52	40
Hearth	32	34	22.75	62	294	38
Fluidized bed and other	14	15	19.29	—	95[(d)]	—
Total or average values	208	221	32.37	67	2360	50

[a] 154 incinerators reporting.

[b] 71 incinerators reporting.

[c] Calculated by multiplying projected number of units × average design capacity × (100 − utilization)/100.

[d] For this projection, average value of 67 percent utilization is used.

[e] Includes units planned and in construction.

may be greatly increased if public opposition exists.

This has created considerable uncertainty for waste generators, equipment manufacturers, and commercial waste disposers. Since 1981, for instance, almost 100 incinerators have withdrawn from the RCRA system because they either ceased operation or decided to no longer handle hazardous wastes.[22] Of the 57 companies identified as marketing hazardous waste incinerators in 1981, 23 have either gone out of business, left the hazardous waste incinerator business, or put considerably less emphasis on this activity.[22]

The amount of public opposition to proposed permits for land-based incinerator facilities varies by location and type of waste. On-site facilities that directly serve a single waste generator have greater public acceptance than off-site, commercial incinerators that serve multiple generators in a large market area. Off-site facilities are often not perceived as providing sufficient economic benefits to the local community to offset the risks associated with the importation of wastes from other areas. On-site facilities are more clearly perceived as being linked to businesses that are important to the local economy, and are generally not perceived as being importers of hazardous waste. Opposition has tended to focus primarily on new off-site facilities, including incinerator ships, and on new applications to burn PCBs, which critics view as particularly hazardous.

In an effort to assess the dilemma of perceived benefits versus public concerns, EPA conducted an assessment in 1985 to determine if there was a need for a change in the approach toward regulating thermal destruction.[3] The major concern reported by citizens included concern for:

- Hazardous material spills in storage, treatment, and handling.
- Environmental and health impacts of land-based and ocean facilities.
- Poor site selection processes.
- Distrust of incinerator owners and operators.
- Inability of government agencies to enforce compliance.

The study concluded that public opposition to both land and ocean incineration may decline somewhat if regulators address more fully some citizen concerns regarding national regulatory strategy, local community impact, equity of facility siting, public decision-making processes, and especially enforcement plans and capacity. It was also concluded that there is a need to better communicate how health and environmental concerns and priorities are reflected in regulations and standards. Better communication of regulatory policy, strategy, and other activity related to decisions on proposed permits for individual incinerator facilities or vessels is certainly desirable since improved communication with the public can enhance the credibility of regulatory and enforcement agencies.

Incineration Technology

Different incineration technologies have been developed for handling the various types and physical forms of hazardous waste. A recent study identified 221 hazardous waste incinerators operating under the RCRA system in the United States.[21] Some of the results of this study are displayed in Table II. The four most common incinerator designs (in order of use) are: liquid injection (sometimes combined with fume incineration); rotary kiln; fixed hearth; and fluidized bed incinerators. These units are located at 189 separate facilities. Only 18 facilities are commercial off-site operations,[31] the balance of incineration practice being located at the site of waste generation.

The process of selection and design of hazardous waste incineration systems can be very complex. Fortunately, considerable industrial manufacturing experience exists and many useful design guides have been published.[7,32–34] Thus, while a detailed examination of design principles is beyond the scope of this paper, a generalized review of the most prominent features of incineration systems and important design factors will be helpful in understanding their operation and emissions performance.

The major subsystems which may be incorporated into a hazardous waste incineration system are:

(1) waste preparation and feeding
(2) combustion chamber(s)
(3) air pollution control
(4) residue/ash handling

The normal orientation of these subsystems is shown in Figure 1 along with typical process component options. The selection of the appropriate system combination of these components is primarily a function of the physical and chemical properties of the waste stream or streams to be incinerated.

(*1*) *Waste Preparation and Feeding.* The physical form of the waste determines the appropriate feed method.[32] Liquids are blended then pumped into the combustion chambers through nozzles or via specially designed atomizing

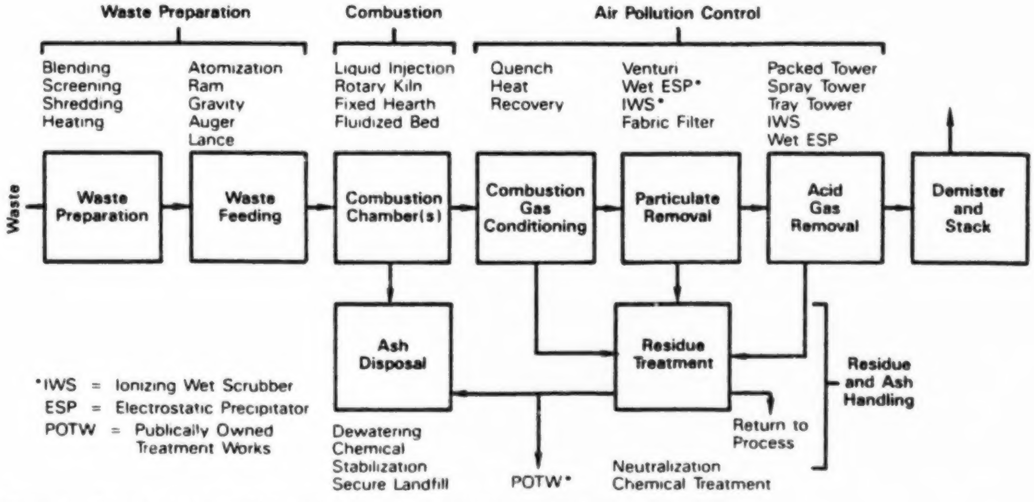
Waste Preparation
Combustion
Air Pollution Control
Blending
Screening
Shredding
Heating
Atomization
Ram
Gravity
Auger
Lance
Liquid Injection
Rotary Kiln
Fixed Hearth
Fluidized Bed
Quench
Heat
Recovery
Venturi
Wet ESP*
IWS*
Fabric Filter
Packed Tower
Spray Tower
Tray Tower
IWS
Wet ESP
Waste
Waste Preparation
Waste Feeding
Combustion Chamber(s)
Combustion Gas Conditioning
Particulate Removal
Acid Gas Removal
Demister and Stack
Ash Disposal
Residue Treatment
Residue and Ash Handling
*IWS = Ionizing Wet Scrubber
ESP = Electrostatic Precipitator
POTW = Publically Owned Treatment Works
Dewatering
Chemical
Stabilization
Secure Landfill
POTW*
Neutralization
Chemical Treatment
Return to Process

Figure 1. General orientation of incineration subsystems and typical process component options.

Table III. Applicability of major incinerator types to wastes of various physical form.[32]

	Liquid injection	Rotary kiln	Fixed hearth	Fluidized bed
Solids:				
Granular, homogeneous		X	X	X
Irregular, bulky (pallets, etc.)		X	X	
Low melting point (tars, etc.)	X	X	X	X
Organic compounds with fusible ash constituents		X		
Unprepared, large, bulky material		X		
Gases:				
Organic vapor laden	X	X	X	X
Liquids:				
High organic strength aqueous wastes	X	X		X
Organic liquids	X	X		X
Solids/liquids:				
Waste contains halogenated aromatic compounds (2,200°F minimum)	X	X		
Aqueous organic sludge		X		X

burners. Wastes containing suspended particles may need to be screened to avoid clogging of small nozzle or atomizer openings. While sustained combustion is possible with waste heat content as low as 4,000 Btu/lb, liquid wastes are typically blended to a net heat content of 8,000 Btu/lb or greater. Blending is also used to control the chlorine content of the waste fed to the incinerator. Wastes with chlorine content of 70 percent and higher have been incinerated,[35] however, most operators limit chlorine content to 30 percent or less.

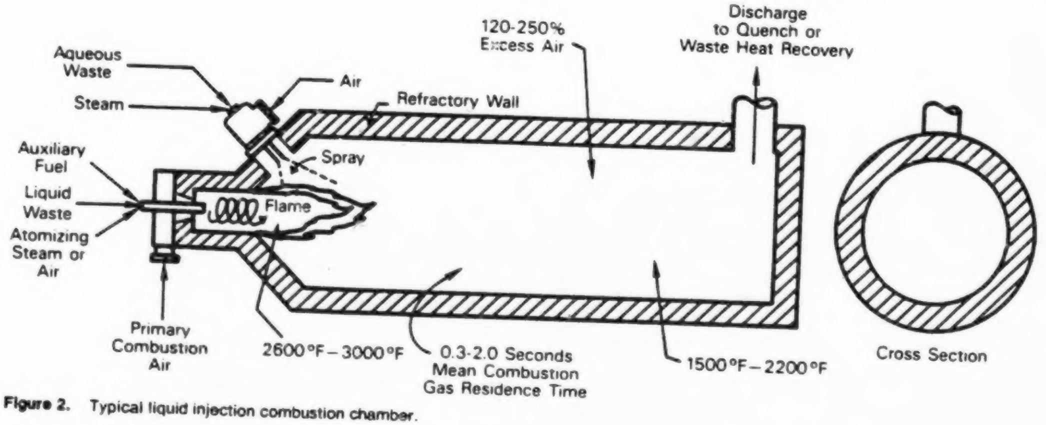

Figure 2. Typical liquid injection combustion chamber.

Blending to these levels provides best combustion control and limits the potential for formation of hazardous free chlorine gas in combustion gases.

Sludges are typically fed using progressive cavity pumps and water cooled lances. Bulk solid wastes may require shredding for control of particle size. They may be fed to the combustion chamber via rams, gravity feed, air lock feeders, vibratory or screw feeders, or belt feeders. Containerized waste is typically gravity or ram fed.

(2) *Combustion Chambers.* The physical form of the waste and its ash content determine the types of combustion chamber selected. Table III provides general selection considerations for the four major combustion chamber (incinerator) designs as a function of wastes of different forms.[32] Most incineration systems derive their name from the type of combustion chamber employed.

Liquid injection incinerators or combustion chambers are applicable almost exclusively for pumpable liquid waste. These units (Figure 2) are usually simple, refractory-lined cylinders (either horizontally or vertically aligned) equipped with one or more waste burners. Liquid wastes are injected through the burner(s), atomized to fine droplets, and burned in suspension. Burners as well as separate waste injection nozzles may be oriented for axial, radial, or tangential firing. Improved utilization of combustion space and higher heat release rates, however, can be achieved with the utilization of swirl or vortex burners or designs involving tangential entry.[36]

Good atomization is critical to achieving high destruction efficiency in liquid combustors. Nozzles have been developed to produce mists with mean particle diameters as low as 1 μm,[37] compared to typical oil burners which yield droplets in the 10- to 50-μm range.[38] Atomization may be attained by low pressure air or steam (1 to 10 psig), high pressure air or steam (25 to 100 psig), or mechanical (hydraulic) means using specially designed orifices (25 to 450 psig).

Vertically aligned liquid injection incinerators are preferred when wastes are high in inorganic salts and fuseable ash content, while horizontal units may be used with low ash waste. The typical capacity of liquid injection incinerators is roughly 28×10^6 Btu/h heat release. Units, however, range as high as 70 to 100×10^6 Btu/h.

Rotary kiln incinerators (Figure 3) are more versatile incinerators in the sense that they are applicable to the destruction of solid wastes, slurries, and containerized waste as well as liquids. Because of this, these units are most frequently incorporated into commercial off-site incineration facility design. The rotary kiln is a cylindrical refractory-lined shell that is mounted on a slight incline. Rotation of the shell provides for transportation of waste through the kiln as well as for enhancement of waste mixing. The residence time of waste solids in the kiln is generally 1 to 1.5 hours. This is controlled by the kiln rotation speed (1–5 revolutions per minute), the waste feed rate and, in some instances, the inclusion of internal dams to retard the rate of waste movement through the kiln. The feed rate is generally adjusted to also limit the amount of waste being processed in the kiln to at most 20 percent of the kiln volume.

The primary function of the kiln is to convert solid wastes to gases, which occurs through a series of volatilization, destructive distillation, and partial combustion reactions. However, an afterburner is necessary to complete the gas-

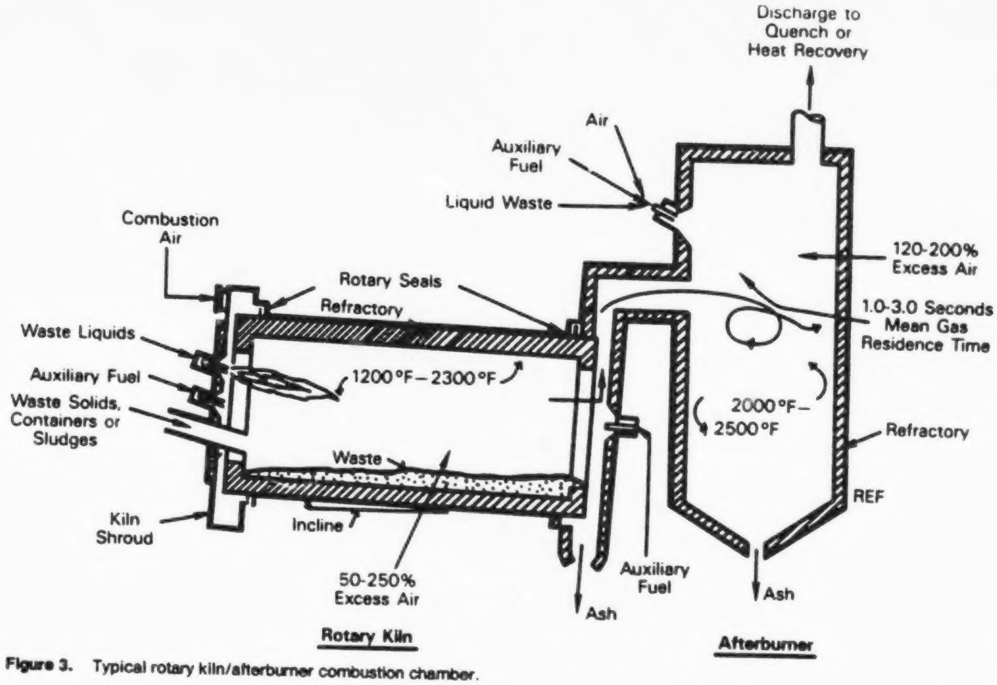
Discharge to
Quench or
Heat Recovery
Air
Auxiliary
Fuel
Liquid Waste
Combustion
Air
Rotary Seals
Refractory
Waste Liquids
Auxiliary Fuel
Waste Solids,
Containers or
Sludges
1200°F–2300°F
Waste
Kiln
Shroud
Incline
50-250%
Excess Air
Rotary Kiln
120-200%
Excess Air
1.0-3.0 Seconds
Mean Gas
Residence Time
2000°F–
2500°F
Refractory
REF
Auxiliary
Fuel
Ash
Ash
Afterburner

Figure 3. Typical rotary kiln/afterburner combustion chamber.

phase combustion reactions. The afterburner is connected directly to the discharge end of the kiln, whereby the gases exiting the kiln turn from a horizontal flow path upwards to the afterburner chamber. The afterburner itself may be horizontally or vertically aligned, and essentially functions much on the same principles as a liquid injection incinerator. In fact, many facilities also fire liquid hazardous waste through separate waste burners in the afterburner. Both the afterburner and kiln are usually equipped with an auxiliary fuel firing system to bring the units up to and maintain the desired operating temperatures. Rotary kilns have been designed with a heat release capacity as high as 90 × 10^6 Btu/h in the United States. On average, however, units are typically 60 × 10^6 Btu/h.

Fixed hearth incinerators, also called controlled air, starved air, or pyrolytic incinerators, are the third major technology in use for hazardous waste incineration today. These units employ a two-stage combustion process, much like rotary kilns (Figure 4). Waste is ram fed into the first stage, or primary chamber, and burned at roughly 50 to 80 percent of stoichiometric air requirements. This starved air condition causes most of the volatile fraction to be destroyed pyrolytically, with the required endothermic heat provided by the oxidation of the fixed carbon fraction. The resultant smoke and pyrolytic products, consisting primarily of volatile hydrocarbons and carbon monoxide, along with products of combustion, pass to the second stage, or secondary chamber. Here, additional air is injected to complete the combustion, which can occur either spontaneously or through the addition of supplementary fuels. The primary chamber combustion reactions and turbulent velocities are maintained at low levels by the starved-air conditions to minimize particu-

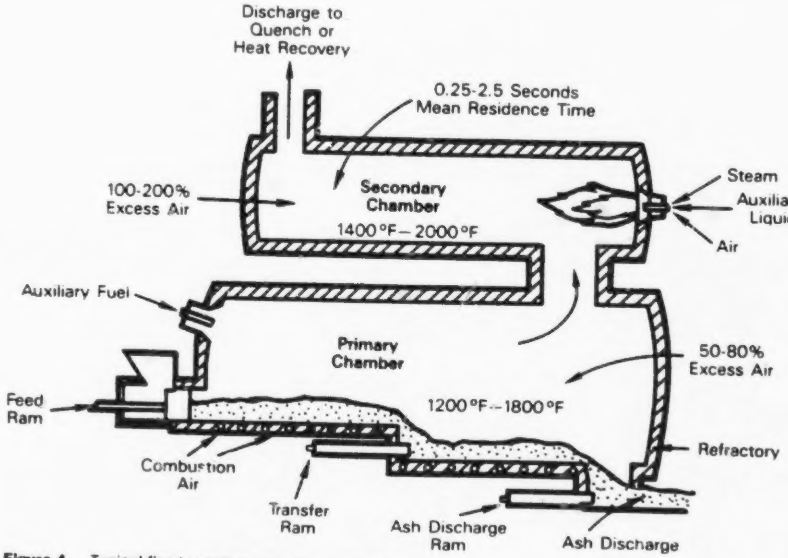
Discharge to
Quench or
Heat Recovery
0.25-2.5 Seconds
Mean Residence Time
100-200%
Excess Air
Secondary
Chamber
1400°F–2000°F
Steam
Auxiliary Fuel or
Liquid Waste
Air
Auxiliary Fuel
Primary
Chamber
50-80%
Excess Air
Feed
Ram
1200°F–1800°F
Refractory
Combustion
Air
Transfer
Ram
Ash Discharge
Ram
Ash Discharge

Figure 4. Typical fixed hearth combustion chamber.

late entrainment and carryover. With the addition of secondary air, total excess air for fixed hearth incinerators is in the 100 to 200 percent range.

Fixed hearth units tend to be of smaller capacity than liquid injection or rotary kiln incinerators because of physical limitations in ram-feeding and transporting large amounts of waste material through the combustion chamber. These lower relative capital costs and potentially reduced particulate control requirements make them more attractive than rotary kilns for smaller on-site installations.

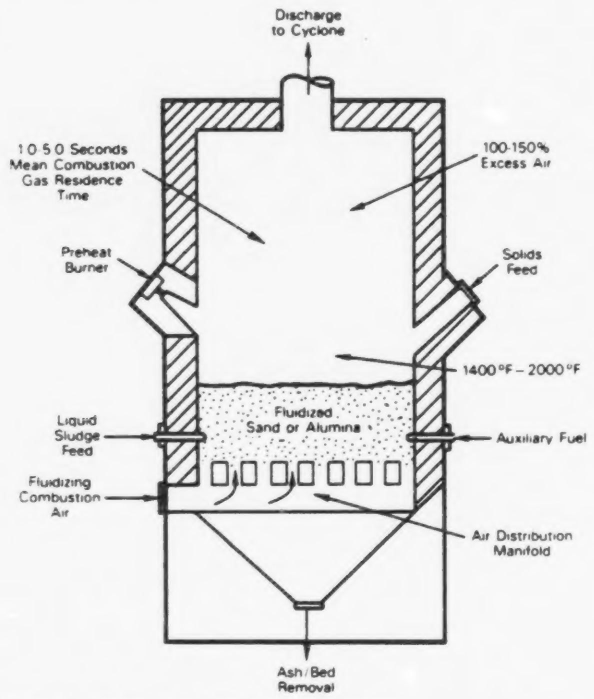

Figure 5. Typical fluidized bed combustion chamber.

Fluidized beds have long served the chemical processing industry as a unit operation. This type of combustion system has only recently begun to see application in hazardous waste incineration. Fluidized bed incinerators may be either circulating or bubbling bed designs.[39] Both types consist of a single refractory-lined combustion vessel partially filled with particles of sand, alumina, sodium carbonate, or other materials. Combustion air is supplied through a distributor plate at the base of the combustor (Figure 5) at a rate sufficient to fluidize (bubbling bed) or entrain the bed material (circulating bed). In the circulating bed design, air velocities are higher and the solids are blown overhead, separated in a cyclone, and returned to the combustion chamber. Operating temperatures are normally maintained in the 1400 to 1600°F range and excess air requirements range from 100 to 150 percent.

Fluidized bed incinerators are primarily used for sludges or shredded solid materials. To allow for good distribution of waste materials within the bed and removal of solid residues from the bed, all solids generally require prescreening or crushing to a size less than 2 inches in diameter. Fluidized bed incinerators offer high gas to solids ratios, high heat transfer efficiencies, high turbulence in both gas and solid phases, uniform temperatures throughout the bed, and the potential for in situ acid gas neutralization by lime or carbonate addition. However, fluid beds also have the potential for solids agglomeration in the bed if salts are present in waste feeds and may have a low residence time for fine particulates.

Regardless of the incinerator type selected, the chemical and thermodynamic properties of the waste determine the sizing of the combustion chamber and its operating conditions (temperature, excess air, flow rates) and determine the nature of air pollution control and ash/residue handling systems. Elemental composition and moisture content data are necessary to determine stoichiometric combustion air requirements and to predict combustion gas flow and composition. These parameters are important in determining combustion temperature and residence time conditions, the efficiency of waste/fuel/air mixing, and in the type and size of air pollution control equipment. Typical operating temperatures, gas (and solid) residence times and excess air rates for each of the four major incinerator types are indicated on Figures 2—5. It is important to understand, however, that significant deviation from these values has been observed in actual field practice without detrimental effect on waste destruction and removal efficiency.[40]

(3) *Air Pollution Control.* Following incineration of hazardous wastes, combustion gases may need to be further treated in an air pollution control system. The presence of chlorine or other halogens in the waste will generally signal a need for a scrubbing or absorption step for combustion gases to remove HCl and other halo-acids. Ash in the waste is not destroyed in the combustion process. Depending on its composition, ash will either exit as bottom ash, at the discharge end of a kiln or hearth for example, or as particulate matter suspended in the combustion gas stream (fly ash). Particulate emissions from most hazardous waste combustion systems generally have particle diameters less than one micron and require high efficiency collection devices to meet the RCRA emission standards. In addition, gas cleaning systems provide some limited additional buffer against accidental releases of incompletely destroyed waste products. Such systems, however, are not a substitute for good combustion and operating practices.

The most common air pollution control equipment employed in hazardous waste facilities is summarized in Table IV.[21] Most often, several of these devices are employed in series. The most common system used is a quench (gas cooling and conditioning), followed by high-energy venturi scrubber (particulate removal), a packed tower adsorber (acid gas removal) and a demister (visible vapor plume elimination). It is interesting to note, however, that more than half of the incinerators employ no air pollution control system at all (Table II). This could be because these facilities are handling low ash, low halogen content liquid waste streams for which such control may not be necessary.

Venturi scrubbers involve the injection of a scrubbing liquid (usually water or a water/caustic solution) into the exhaust gas stream as it passes through a high velocity con-

Table IV. Distribution of air pollution control devices (APCD) among hazardous waste incinerators.[a]

APCD type	Number	Percent
Quench	21	23.3
Venturi scrubber	32	35.6
Wet scrubber	7	7.8
Wet ESP	5	5.5
Ionizing wet scrubber	5	5.5
Other non-specified scrubber	12	13.3
Packed tower absorber	18	20.0
Spray tower absorber	2	2.2
Tray tower absorber	1	1.1
Other absorbers	2	2.2
None/unknown	31	34.4
Total incinerator systems surveyed	90	

[a] Total number of APCD types are greater than systems surveyed as many incinerators report more than one APCD.

striction, or throat. The liquid is atomized into fine droplets which entrain fine particles and a portion of the absorbable gases in the gas stream. The major advantage of venturi scrubbers is their reliability and relative simplicity of operation. On the other hand, maintaining the significant pressure drop across the venturi throat (60 to 120 inches of water column) required for hazardous waste combustion particulate matter control represents a significant percentage of the total cost of operation of incineration facilities employing venturi scrubbing.

Acid gas removal is generally accomplished in packed bed or plate tower scrubbers. Packed bed scrubbers are generally vessels filled with randomly-oriented packing material such as polyethlyene saddles or rings. The scrubbing liquid is fed to the top of the vessel, with the gas flowing in either concurrent, countercurrent, or crossflow modes. As the liquid flows through the bed, it wets the packing material and thus provides the interfacial surface area for mass transfer with the gas phase which is required for effective acid gas absorption.

Like packed bed scrubbers, plate scrubbers also rely on absorption for the removal of contaminants. The basic design is a vertical cylindrical column with a number of plates or trays inside. The scrubbing liquid is introduced at the top plate and flows successively across each plate as it moves downward to the liquid outlet at the tower bottom. Gas comes in at the bottom of the tower and passes through openings in each plate before leaving through the top. Gas absorption is promoted by the breaking up of the gas phase into small bubbles which pass through the volume of liquid in each plate.

Packed bed or plate tower scrubbers are commonly used at liquid injection incinerator facilities, where absorption of soluble gaseous pollutants (HCl, SO_x, NO_x) is most important and particulate control is less critical. However, at rotary kiln or fixed hearth facilities, or liquid injection facilities where high ash content wastes are incinerated, venturi scrubbers are often used in series with packed bed or plate tower scrubbers.

Many designs in recent years have begun to incorporate waste heat boilers as a substitute for gas quenching and as a means of energy recovery.[41,42] Wet electrostatic precipitators (ESP) ionizing wet scrubbers (IWS) and fabric filters are also being incorporated into newer systems[43] largely due to their high removal efficiencies for small particles and lower pressure drop.

(4) *Residue and Ash Handling.* The inorganic components of hazardous wastes are not destroyed by incineration. These materials exit the incineration system either as bottom ash from the combustion chamber, as contaminants in scrubber waters and other air pollution control residues, and in small amounts in air emissions from the stack. Under RCRA, residues generated from the incineration of hazardous waste should be managed carefully.

Ash is commonly either air-cooled or quenched with water after discharge from the combustion chamber. From this point ash is frequently accumulated on-site in storage lagoons or in drums prior to disposal in a permitted hazardous waste land disposal facility. Dewatering or chemical fixation/stabilization may also be applied prior to disposal.

Air pollution control residues are generated from the combustion gas quenching, particulate removal and acid gas absorption steps in an incineration system. These residues are typically aqueous streams containing entrained particulate matter, absorbed acid gases (usually as HCl) and small amounts of organic contaminants. These streams are often collected in sumps or recirculation tanks where the acids are neutralized with caustic and returned to the process. Eventually, a portion or all of these waters must be discharged for treatment and disposal (generally when the total dissolved solids level exceeds 3 percent). Many facilities discharge neutralized waters to settling lagoons or a chemical precipitation step to allow for suspended contaminants to be concentrated and ultimately sent to land disposal. Depending upon the nature of the dissolved contaminants and their concentration after treatment, waters may either be returned to the process or discharged to sewers.

Other Hazardous Waste Thermal Destruction Systems

Other types of systems are also being employed to thermally destroy hazardous waste. These include: ocean incineration vessels, mobile incinerators, and high temperature industrial furnaces.

Ocean incineration involves the thermal destruction of liquid wastes at sea in specially designed tanker vessels outfitted with high-temperature incinerators. The principle of operation of these units is identical to that of land-based liquid injection incinerators with the exception that current ocean incinerators are not equipped with air pollution control systems. Acid gas produced from incinerating chlorinated wastes is discharged to the air without treatment to be neutralized by contact with sea water, which has a naturally high buffering capacity.

Ocean incineration has been routinely used in Europe since 1969.[44] A total of six different vessels have conducted hundreds of waste burns in the North Sea. Although several test burns and research studies involving herbicide orange, mixed organo-chlorine waste and PCBs have occurred under United States sponsorship ocean incineration has never been used on a routine commercial basis in the United States.[45] This has been largely due to vocal public concern over potential environmental effects that could result from incinerator emissions and spills of hazardous materials during loading and transport of wastes.

The importance of ocean incineration, however, is not that it is currently a major factor in the United States hazardous waste management but, rather, that it has served as a focal point for public and scientific debate over the state of knowledge of the character and potential effects of emissions from incineration processes in general. These issues have been explored in several major studies on ocean and land-based incineration conducted over the past two years[30,46,47]. While these studies have found incineration to be the most effective technology currently available for organic hazardous waste destruction, many of the important technical and policy issues examined will significantly impact the direction of incineration practice and research over the next decade.

A number of companies are marketing mobile or transportable incineration systems. Most of these are scaled-down, trailer-mounted versions of conventional rotary kiln or fluidized bed incinerators. The thermal capacities of most mobile systems range from 10 to 20 million Btu/h.

The first mobile rotary kiln incinerator was designed and tested by EPA as a potential solution to on-site clean-up at uncontrolled waste sites.[19,48] Other rotary kiln systems have since been developed and employed at waste sites.[19,49–51] Mobile fluidized bed systems are also being marketed.[52]

Overall, the performance of these mobile systems has been shown to be comparable to equivalent stationary facilities. Current experience suggests, however, that waste incineration is more expensive in mobile units, on a unit cost basis, than it is in stationary units. The principal advantage of mobile systems appears to be that they are more socio-politically acceptable than removal and transportation of clean-up residues to commercial facilities. In the instance of soil decontamination, on-site incineration may also be more cost-effective than transportation of large amounts of contaminated material to central incineration facilities.

More substantial than either ocean or mobile incineration practice is the use of hazardous wastes as fuels in industrial boilers and furnaces. In 1981, these operations disposed of more than twice the amount of waste that was disposed of via incinerators.[2] Processes that have burned or do burn hazardous waste materials as fuels include: industrial boilers, cement kilns, iron-making furnaces, and light-weight aggregate and asphalt plants. The principal attractions to this approach include: exemption (currently) from RCRA incineration standards, fuel and waste transportation cost-savings, and waste disposal cost savings since hazardous waste used as a fuel can be sold.

The most recent source of information on waste fuel use in industrial processes was compiled for EPA in 1984.[53] The study synopsizes results of a national questionnaire of waste fuel and waste oil use in 1983. The study revealed that there were over 1,300 facilities using hazardous waste-derived fuels (HWDF), accounting for a total of 230 million gallons per year. The chemical industry (Standard Industrial Classification 28) accounted for 67 percent of this while operating only 12.4 percent of the facilities using HWDF. Other industries employing significant quantities of hazardous waste as fuel included: SICs 26 (paper), 29 (petroleum), 32 (stone, clay, glass, concrete), and 33 (primary metals). The majority (69 percent) of the waste was burned in large quantities by a few facilities representing only a small fraction (1.6 percent) of the 1,300 facilities. These included medium- to large-sized industrial boilers, cement and aggregate kilns, and iron-making furnaces.

While waste code-specific data on HWDF are not readily available, recent data indicate that of the HWDF burned in 1983, 30 percent was organic solvents, and 45 percent was other hazardous organics.[53] Most of this waste was generated on-site and 74 percent of the balance arrived directly from an off-site generator rather than through an intermediary.

Measuring Process Performance

Proper and accurate measurement of the emissions from incineration systems is a critical issue. Great demands have been placed upon sampling and analysis technology by the RCRA incinerator regulations. Fortunately, significant progress has been made in adopting measurement methods to the rigors of specific compound identification and the level of detection and accuracy which are often necessary to assess compliance with the RCRA incineration standards. These methods will rarely be a limitation in assessing incinerator performance if proper attention is given to quality assurance and quality control, adequate advanced planning is conducted, and experienced personnel are involved in sampling and analysis activities.

Performance measurement may have any of the following three purposes:

- to establish compliance with performance standards (e.g., trial burns)
- to monitor process performance and direct process control (e.g., continuous monitoring)
- to conduct performance measurements for research and equipment development purposes

Methods employed in assessing regulatory compliance are generally official methods which have been standardized and published in the *Federal Register* or in EPA guidance documents. Routine performance monitoring for process control often involves the use of continuous monitors for emissions and facility-specific engineering parameters (e.g., temperature, pH, kiln rotation). Research and equipment assessment investigations may involve any of the above techniques in combination with standard and often nonstandard sampling and analysis techniques designed for rapid screening of performance or for ultra-low detection of specific materials.

Performance Measurement

Figure 6 illustrates sampling points which may be involved in assessing incinerator performance. In the case of trial burn activities, the main focus of sampling activities is on collection of waste feed and stack emission samples. Ash

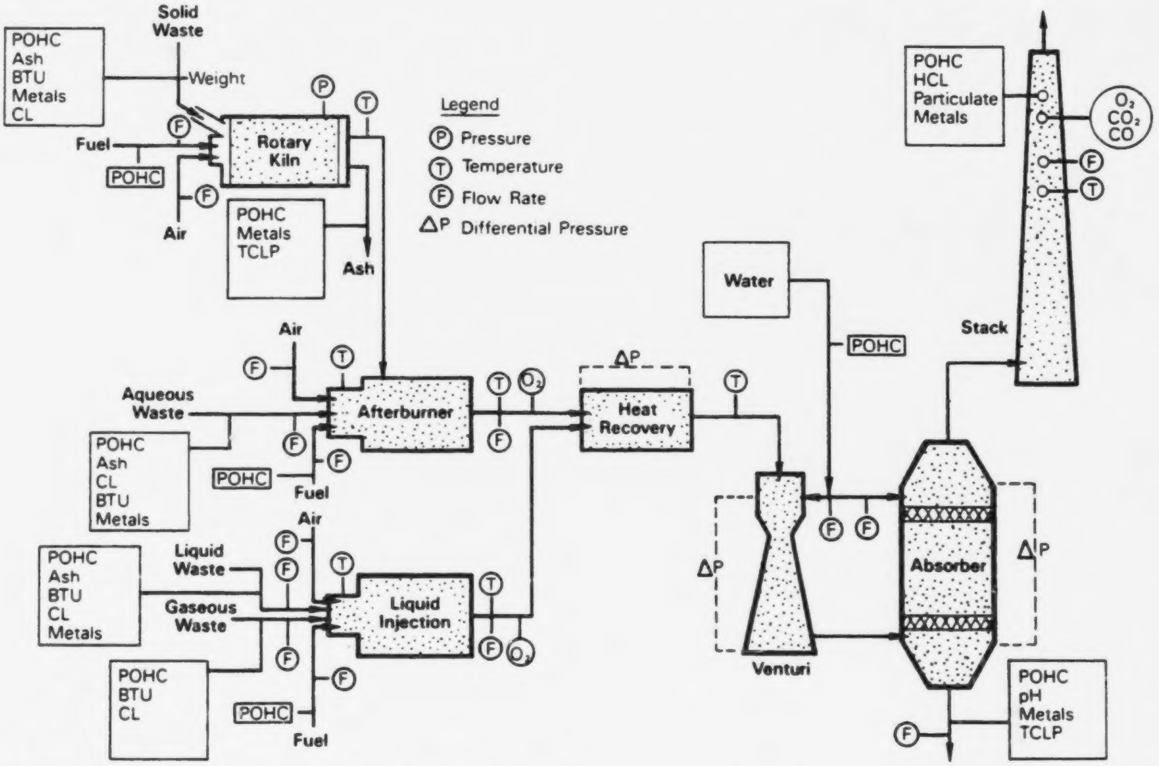

Figure 6. Potential sampling points for assessing incinerator performance

Table V. Sampling methods and analysis parameters

Sample	Sampling frequency for each run	Sampling method[a]	Analysis parameter[b]
1. Liquid waste feed	Grab sample every 15 min	S004	V&SV-POHCs, Cl^-, ash, ult. anal., viscosity, HHV
2. Solid waste feed	Grab sample from each drum	S006, S007	V&SV-POHCs, Cl^-, ash, HHV
3. Chamber ash	Grab one sample after all 3 runs are completed	S006	V&SV-POHCs, TCLP[d]
4. Stack gas	Composite	MM5 (3 h)	SV-POHCs, particulate, H_2O, HCl
	Three pairs of traps 40 min each pair	VOST (2 h)	V-POHCs
	Composite in Tedlar gas bag	S011	V-POHCs[c]
	Compounds in mylar gas bag	M3 (1–2 h)	CO_2 and O_2 by Orsat
	Continuous (3 h)	Continuous monitor	CO (by plant's monitor)

[a] VOST denotes volatile organic sampling train; MM5 denotes EPA Modified Method 5; M3 denotes EPA Method 3; SXXX denotes sampling methods found in "Sampling and Analysis Methods for Hazardous Waste Combustion." [55]

[b] V-POHCs denotes volatile principal organic hazardous constituents (POHCs); SV-POHCs denotes semivolatile POHCs; HHV denotes higher heating value.

[c] Gas bag samples may be analyzed for V-POHCs, only if VOST samples are saturated and not quantifiable.

[d] TCLP—toxicity characteristic leaching procedure.[58]

and air pollution control system residues are also sampled and analyzed. Sampling of input/output streams around individual system components (e.g., scrubbers) may also be conducted in research testing or equipment evaluation studies.

The main focus of analytical activities is on POHCs. Stack gas analysis also includes determination of HCl and particulate emissions, and may be extended to a determination of other organic compound emissions as well as metals of concern. In the case of particulate emissions, the size distribution of stack particles may also be of interest. The size of emitted particulate affects its transportation and fate in the atmosphere and influences the likelihood of inhalation, an important factor in health effects assessment. Few hazardous waste incinerator tests have actually collected particle size data, primarily due to time and funding limitations.

EPA has provided guidance on the types and methods of sampling and analysis to be used in trial burns designed to measure facility compliance with the RCRA incinerator standards.[54,55] Additional guidance is being prepared. Similar guidance has also been provided for PCB incinerators.[56] Table V outlines sampling and analysis methods typically involved in RCRA trial burns. For any trial burn, at any one set of operating conditions and waste feed conditions, three replicate runs (i.e., identical as possible) are usually recommended to obtain a representative assessment of incinerator performance.[55]

The sampling method numbers in Table V refer to methods identified in a manual of combustion sampling and analysis methods compiled by EPA.[57] This manual expands upon and augments the information in EPA SW-846, "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods"[59] and "Samplers and Sampling Procedures for Hazardous Waste Streams."[60] Together, these references are the best sources from which to identify methods to be used in incinerator performance evaluations.

Analytical methods for specific hazardous compounds are often of greatest interest. Analytical methods for Appendix VIII compounds[10] in these references are generally based upon high-resolution fused-silica-capillary column gas chromatography (GC) in combination with mass spectrometry (MS) for specific compound detection. High-performance liquid chromatography (HPLC) is recommended for determination of compounds that are inappropriate for detection by GC/MS. Application of analytical methods has been evaluated for 240 of the approximately 400 Appendix VIII Compounds.[61,62] The methods showed acceptable precision in determination of most of the compounds. Detection limits in synthetic samples were on the order of 1 to 10 nanograms per injection, but detection in actual waste samples will be dependent upon the nature of interferences in the waste matrix.

While all emissions from hazardous waste incinerators are important, the greatest interest is most often placed on stack emissions. The accuracy and reliability of stack sampling results are central to the entire issue of incinerator performance and environmental safety. Existing methods have been the subject of substantial research, debate and, in some cases, criticism.[63]

Stack emissions are sampled to determine stack gas flow rate, HCl, particulate concentration and the concentration of organic compounds of interest. Determination of stack gas flow rate and particulate emissions is performed using the conventional stack sampling method commonly referred to as Method 5 (M5). This method encompasses EPA Methods 1 through 5 and is defined in detail in 40 CFR Part 60, Appendix A. HCl emissions are sampled by modifying the Method 5 train to include a caustic impinger. A specialized sampling and analytical method has also been developed to further speciate and quantify hydrogen halide and halogen emissions.[64]

The technology of incinerator stack sampling for trace organic compounds is sophisticated. While the basic technology is well developed, many pitfalls await those who attempt the job without sufficient knowledge or experience. Sampling of stack effluent for organics, in order to determine DRE, may require from one to three separate methods (or more), depending on the number of compounds to be quantified and their characteristics, and on the detection limits that are required to prove a DRE of 99.99 percent or establish levels of incomplete combustion byproducts. Special attention must be given to sampling rate and duration in planning for emission tests to insure that a sufficient amount of sample is collected to meet detection limit objectives and to allow for all necessary analyses to be completed.[55]

The three methods for hazardous waste incinerator sampling are:

1. Modified Method 5 (MM5)
2. Volatile Organic Sampling Train (VOST)
3. Gas bags

The Modified Method 5 (MM5) train is used to capture semivolatile (boiling point 100°C to 300°C) and non-volatile (boiling point >300°C) organic compounds. The MM5 is merely a simple modification of the M5 train involving insertion of a sorbent module (XAD-2 resin) between the filter and the first impinger.[65] It is recommended that a separate M5 train for particulate determination be used in tandem with the MM5 train since drying of the filter for particulate determination may invalidate analysis of organic compounds on the filter.[55] Like the M5, the MM5 involves isokinetic traversing of the stack with a sampling probe. Water-cooled sample probes are necessary for sampling of hot combustion gases in regions ahead of quenching. Where it is desirable to collect larger amounts of sample for more extensive analysis or lower detection limits, the much larger Source Assessment Sampling System (SASS) may be used instead of the MM5.[55] SASS involves single point (pseudo-isokinetic) sampling at a rate of 110 to 140 L/min (4 to 5 cfm) compared to the 14 to 28 L/min (0.5 to 1 cfm) rate of the MM5. The same sorbent resin (XAD-2) is also used. Because of its more convenient sample size and portability, and its multipoint isokinetic sampling the MM5 train is generally preferred over the SASS train.

For volatile organic compounds (boiling point 30°C to 130°C), the Volatile Organic Sampling Train (VOST) is used. The VOST was developed by EPA in 1981 to enable detection of stack concentrations of volatile organic compounds as low as 0.1 ng/L.[66] This detection limit was deemed necessary to be able to demonstrate greater than 99.99 percent DRE for volatile organic compounds at concentrations as low as 100 ppm in the waste feed. The VOST system involves drawing a single stack gas sample through two sorbent tubes in series. The first tube contains Tenax resin and the second, Tenax and activated charcoal. Up to six pairs of sorbent tubes operating at one L/min for 20 minutes each may be needed to achieve the lowest detection levels.[67] For higher stack gas concentrations, however, the VOST may be operated at lower flow rates with less pairs of tubes (longer sampling times for each pair).

Various types of gas sampling bags may also be used to sample for volatile organic compounds. These are generally appropriate only for higher organic concentrations. The accuracy of sampling with this method is a function of the sampling and storage characteristics of the bags.[68] The use of extensive quality assurance and quality control procedures is required with both plastic bags and the VOST to avoid sample contamination in the field and in transit.[69] This problem was not fully appreciated in some of the early field tests employing the VOST.

Both the MM5 and VOST sampling methods have been subjected to laboratory and field validation studies for selected compounds.[70-72] These studies have demonstrated that excellent results are possible with these methods. It is important to note, however, that modifications of these methods may be required for certain POHC compounds which become chemically or physically altered in the sampling systems. Highly water soluble compounds (e.g., acetonitrile) and water-reactive compounds (e.g., phthalic anhydride), for instance, present special challenges to current sampling methods.

Table VI. Summary of continuous emission monitors.

Pollutant	Monitor type	Expected concentration range	Available range[a]
O_2	Paramagnetic	5–14%	0–25%
	Electrocatalytic (e.g., zirconium oxide)		
CO_2	NDIR[b]	2–12%	0–21%
CO	NDIR	0–100 ppm	0–5000 ppm
NO_x	Chemiluminescent	0–4000 ppm	0–10000 ppm
SO_2	Flame photometry	0–4000 ppm	0–5000 ppm
	Pulsed fluorescence		
	NDUV[c]		
SO_3	Colorimetric	0–100 ppm	0–50 ppm
Organic compounds	Gas chromatography (FID)[d]	0–50 ppm	0–100 ppm
	Gas chromatography (ECD)[e]		
	Gas chromatography (PID)[f]		
	IR absorption		
	UV absorption		
	GC/MS		

[a] For available instruments only. Higher ranges are possible through dilution.

[b] Nondispersion infrared.

[c] Nondispersion ultraviolet.

[d] Flame ionization detector.

[e] Electron capture detector.

[f] Photo-ionization detector.

Process Monitoring

Measurement of a wide variety of incinerator operating parameters may be necessary to maintain thermal destruction conditions which are equivalent to those observed during a successful trial burn. These measures are used as indicators of the performance of the incineration system and serve as input to automatic and manual process control strategies. There are nearly two dozen potential measurements, including such parameters as: combustion temperature, waste feed rate, oxygen and carbon monoxide (CO) concentration in the stack, gas flow rate at strategic points, and scrubber solution pH. These parameters and their use are described in detail in a number of resource documents.[32,54,55,73]

Continuous emission monitors (CEM) are often used or required in measuring combustion gas components such as carbon monoxide (CO), oxygen (O_2), nitrogen oxides (NO_x), and total unburned hydrocarbons (TUHC). If properly interpreted, combustion gas components may be indicators of the completeness of the thermal destruction reaction. These methods typically require extraction of gas samples from the gas stream of interest and measurement with a remote instrument. Some parameters such as CO and O_2 may be measured in-situ (in the stack). Table VI summarizes monitor types, and available concentration measurement ranges for a number of CEMs.[74]

RCRA incinerator operating requirements stipulate that the permit specify an operating limit for CO concentration in the stack gas. While continuous CO monitoring is required, specific CEM requirements are not specified. However, permit writers frequently cite Reference Method 10 from the EPA New Source Performance Standard (NSPS) as a guide (40 CFR 60, Appendix A). CO concentration in stack gas is an indicator of combustion efficiency. However, this parameter is also being examined as a possible real-time indicator of DRE for hazardous organic compounds.

Total unburned hydrocarbon (TUHC) emissions are also being considered as a possible DRE indicator. Three types of analyzers are available: flame ionization detector (FID), photo-ionization detector (PID); and, the automated total gaseous nonmethane organics analyzer (TNMO). FID is used most typically. All three methods have limitations. The theoretical minimum detectability of all three techniques in significantly below 10 μg/dscf (detection in the 10 to 700 μg dscf would be required for DRE correlation purposes). However, due to electrical noise, sampling limitations and component degradation, the practical field detectability limit is from 40 μg/dscf to 200 μg/dscf, if care is exercised.[74] The individual methods are also limited by the fact they do not respond to all classes of organic compounds of potential concern.

Table VII. Incinerator performance and stack emissions data (data reported as averages for each facility).

Facility type	O_2 (%)	CO (ppm)	TUHC (ppm)	DRE (%)	Particulate (mg/m^3)	HCl control (%)
Commercial rotary kiln/ liquid incinerator	10.5	6.2	1.0	99.999	152	99.4
Commercial fixed hearth, two-stage incinerator	11.4	6.9	1.0	99.994	400	98.3
On-site two-stage liquid incinerator	8.1	9.4	6.0	99.994	143	99.7
Commercial fixed hearth, two-stage incinerator	11.0	327.7	18.7	99.997	60	b
On-site liquid injection incinerator	13.2	11.9	1.0	99.999	186	b
Commercial two-stage incinerator	10.2	1.1	1.3	99.998	902	b
On-site rotary kiln incinerator	9.7	554.0	61.7	99.999	23	99.9
Commercial two-stage fixed hearth incinerator	13.4	26.8	1.8	99.996	168	98.3
On-site rotary kiln	c	794.5	NA[a]	99.998	184	99.7
On-site liquid injection incinerator	9.7	66.3	7.8	99.994	95	b
On-site rotary kiln incinerator	10.7	5.8	NA	99.996	404	99.9
On-site rotary kiln incinerator	14.1	323.0	NA	99.996	NA	99.8
On-site liquid injection incinerator	12.4	31.9	1.9	99.999	163	98.6
On-site liquid injection incinerator	9.3	1.0	NA	99.996	40	b
On-site fluidized bed incinerator	3.6	67.4	NA	99.996	259	b
On-site fixed hearth incinerator	12.9	ND[d]	NA	99.999	93	b
On-site liquid injection incinerator	4.5	358.0	NA	99.995	99	b
On-site liquid injection incinerator	3.6	28.4	NA	99.998	12	99.3
Commercial rotary kiln incinerator	9.4	8.0	0.5	99.999	172	99.9
On-site liquid injection incinerator	3.1	779.3	NA	99.999	88	99.6
On-site liquid furnace incinerator	6.4	56.3	NA	99.999	4	99.9
On-site fixed hearth incinerator	13.5	5.0	NA	99.999	150	98.4

NA—not available.

[b] HCl emissions <4 lb/h.

[c] Reported only as a range (3.1–16.7%).

[d] Not detected.

Emissions from Hazardous Waste Incineration

Ideally, the primary products from combustion are carbon dioxide, water vapor, and inert ash. In reality, what appears outwardly to be a straightforward, simple process is actually an extremely complex one involving thousands of physical and chemical reactions, reaction kinetics, catalysis, combustion aerodynamics, and heat transfer. This complexity is further aggravated by the complex and fluctuating nature of the waste feed to the process. While combustion and incineration devices are designed to optimize the chances for completion of these reactions, they never completely attain the ideal. Rather, small quantities of a multitude of other products may be formed, depending on the chemical composition of the waste and the combustion conditions encountered. These products along with potentially unreacted components of the waste become the emissions from the incinerator.

Hydrogen chloride (HCl) and small amounts of chlorine (Cl_2), for example, are formed from the incineration of chlorinated hydrocarbons. Hydrogen fluoride (HF) is formed from the incineration of organic fluorides, and both hydrogen bromide (HBr) and bromine (Br_2) are formed from the incineration of organic bromides. Sulfur oxides (SO_x), mostly as sulfur dioxide (SO_2), but also including 1 percent to 5 percent sulfur trioxide (SO_3), are formed from the sulfur present in the waste material and auxiliary fuel. Highly corrosive phosphorus pentoxide (P_5O_5) is formed from the incineration of organophosphorus compounds. In addition, oxides of nitrogen (NO_x) may be formed by fixation of nitrogen from nitrogen compounds present in the waste material or in the combustion air. Suspended particulate emissions are also produced and include particles of mineral oxides and salts from the mineral constituents in the waste material. A wide range of organic compounds may also be formed from the incomplete thermal destruction of organic compounds in the waste and auxilary fuel.

Until recently, there were only limited data available on waste destruction performance and pollutant emissions from hazardous waste thermal destruction devices. Studies by EPA and others in the early to late 1970s employed a variety of evolving trace organic pollutant sampling and analysis techniques and were often targeted only towards measuring macro-destruction and combustion efficien-

Table VIII. Summary of boiler performance.

Facility type	Load (%)	O_2(%)	Residence time (s)	Average volumetric heat release rate (kW/m^3)	DRE[d]	W/F[a] (%)	NO_x (ppm)[b]	CO (ppm)[b]
Watertube stoker	100	6–16	1.2	509	99.98	40	163–210	900–1200
Packaged firetube	25	4–6	0.8	739	99.991	0.1–0.5	40–65	47–88
Field erected watertube	26	10	2	78	99.999	37	61–96	18–21
Converted stoker	78	4–6	1.1	339	99.998	18–48	193–250	75–127
Packaged watertube	36–73	6–7	1.1–0.5	960	99.995	19–56	164–492	83–138
Converted watertube	53	7–11	2	107	99.98	8.7–10.1	243–328	109–139
Modified firetube	44	8	0.4	807	99.998	100	67–74	146–170
Tangentially fired watertube	100	6	2	180	99.991	2.4–4.3	393–466	142–201
Packaged watertube	65	2	1.8	343	99.998	8.2	64–78 410–1125[c]	46–750
Packaged firetube	50–100	3–8	0.7–0.3	1240	99.999	100	85–203	20–135
Packaged watertube	82	4	1.8	269	99.999	49	154–278	102–119

[a] W/F = waste heat input as a percent of total heat input.
[b] Range of average values across individual sites and runs including baseline.
[c] Higher values are for high nitrogen content waste firing.
[d] Mass weighted average for all POHCs in the waste >100 ppm.

cies,[75–77] rather than the performance standards now required under the Resource Conservation and Recovery Act of 1976. Since 1981, however, EPA has conducted a substantial program of performance testing at thermal destruction facilities. The testing was designed to estimate the environmental impact of these operations and to provide information on the ability of these facilities to control emissions to the degree required by the 1982 incinerator performance standards. The test facilities, test procedures and performance results have been summarized[78] for the facilities tested (incinerators, industrial boilers and industrial process kilns). Complete test reports have been published for the incinerators,[79] industrial boilers,[80,81] and cement/aggregate kilns[82,83] tested. These data as well as trial burn results from 14 additional RCRA incinerators have been summarized recently in an EPA report, "Permit Writer's Guide to Test Burn Data—Hazardous Waste Incineration."[84]

The following sections summarize these data in five areas:

- RCRA-regulated performance and emissions (DRE, particulate matter, and HCl)
- Metal emissions
- Combustion by-product emissions
- Dioxin and furan emissions
- Ash and air pollution control residue quality

RCRA Regulated Performance and Emissions

Tables VII, VIII, and IX summarize waste destruction efficiency, HCl and particulate emissions results for the incinerators, industrial boilers, and cement kilns tested. The tables also summarize certain process operating parameters as well as emissions of CO and O_2 and, in some instances NO_x and SO_x.

These data reveal that well operated incinerators, industrial boilers, and process kilns are capable of achieving a 99.99 percent DRE, the RCRA performance standard. All of the incinerators tested by EPA achieved this level of performance for candidate POHC compounds in concentrations greater than 1200 parts per million (ppm) in the waste feed.[85] Candidate POHC compounds between 200 and 1200 ppm frequently were not destroyed to a 99.99 percent DRE and no compounds below 200 ppm in the waste feed met the RCRA DRE limit. In fact, regression analysis of the pooled

Table IX. Summary of industrial kiln performance and stack emissions data (data reported as averages for each facility).

Facility type	Test[a]	DRE (%)	Particulate (kg/MG)[c]	HCl (kg/h)	NO_x (ppm)	SO_2 (ppm)	W/F(%)[b]
Wet process cement kiln	W	99.200	0.27	0.36	68	450	25
(non-atomized waste)	B	—	0.26	0.09	136	279	—
Wet process cement kiln	W	99.996	0.27	2.1	478	265	15
(atomized waste)	B	—	0.26	0.6	371	636	—
Dry process cement kiln	W	99.998	—	11.5	814	19	45
(non-atomized waste)	B	—	—	1.3	620	7	—
Dry process cement kiln	W	99.992	—	0.47	486	27	15
(atomized waste)	B	—	—	0.25	680	27	—
Lime kiln	W	99.997	0.11	0.20	446	596	30
(atomized waste)	B	—	0.10	0.09	386	553	—
Shale aggregrate kiln (atomized waste)	W	>99.99	0.33	2.1	—	—	100
Clay aggregate kiln (atomized waste)	W	99.998	0.58	0.023	162	1130	59
Clay products kiln (atomized waste)	W	>99.99	0.002	0.84	—	—	100

[a] W = waste testing, B = baseline (fossil fuel only).
[b] W/F = waste fuel heat input expressed as a percent of total heat input.
[c] Particulate emissions are expressed as kg particulate per metric ton (MG) of product produced (e.g., cement, lime).

Table X. Average stack emissions of metals from five hazardous waste incinerators.[a]

Metals	Emission rate (g/kJ) and concentration on particulate (μg/g)[b]					
	Plant A	Plant B uncontrolled	Plant B controlled	Plant C	Plant D	Plant E
Sb	0.32 (8,380)[b]	0.26 (300)	c	c	—	—
As	—	c	c	c	—	d
Be	0.052 (840)	0.19 (250)	0.11 (930)	c	0.056 (1,490)	0.050 (470)
Be	—	(5)[c]	c	c	—	d
Cd	0.055 (890)	0.11 (140)	0.019 (150)	c	0.012 (1,120)	0.36 (4,000)
Cr	0.14 (2,300)	0.73 (950)	0.19 (1,500)	2.5 (47,500)	d	0.094 (1,100)
Pb	5.4 (85,500)	2.3 (3,100)	0.64 (5,300)	c	0.24 (25,600)	9.0 (98,000)
Ng	d	c	c	c	—	—
Ni	0.024 (400)	0.50 (650)	0.087 (740)	2.7 (49,000)	0.052 (4,570)	d
Se	—	7.0 (9,200)	0.45 (3,700)	c	0.29 (34,600)	—
Ag	0.0008 (11.4)	c	c	0.33 (620)	0.0076 (917)	—
Ti	0.0089 (140)	c	c	c	—	—

[a] Adapted from Wallace *et al.*, 1985.[97]

[b] Numbers in parentheses represent values for μg of metal/g of emitted particulate.

[c] All values below detection limit.

[d] Some values below detection limits, average not calculated.

[e] Emissions are reported as gram of particulate emitted per hour divided by the design heat release rate of the incinerator in kJ/h.

data suggested that statistically significant correlations (correlation coefficients were 0.76 and 0.84) existed between compound penetration (1-DRE) and compound feed concentration, showing that DRE increased with waste feed concentration.[85]

This phenomenon, which has been observed in tests of other thermal destruction devices, was not anticipated. A number of possible explanations have been advanced.[2,79] The most frequently stated theory postulates that at the very low stack emission concentrations (<1 ng/L) necessary to demonstrate greater than 99.99 percent DRE for a sub-1200 ppm compound, sufficient amounts of that compound may actually be formed as an incomplete combustion or recombination byproduct from other compounds in the wastes to effect a reduction of the DRE below 99.99 percent. Others argue that limitations of current stack sampling and analysis techniques for such low levels of trace organic compounds are responsible.

EPA is conducting research to assess this concentration phenomenon. From a regulatory standpoint, however, this is not currently perceived as an issue. Few, if any, of the low concentration compounds in the wastes identified in the EPA test program would have actually been selected as "principal" organic hazardous constituents in trial burns if existing EPA guidance on POHC selection were employed. It is also important to note that even though DRE declines with lower initial compound concentrations in the waste, the amount absolute of compound emitted also declines. In fact, the DRE vs. concentration correlation noted above actually predicts that the net emissions resulting from a reduced DRE for a 100 ppm compound will actually be slightly less than those for a 99.99 percent DRE for the compound at 1000 ppm in the waste.

Table VIII indicates that industrial boilers, particularly the larger water tube units, typically attain 99.99 percent DRE. Cement kilns, lime kilns, and light weight aggregate kilns with good combustion control and waste atomization all met or exceeded the 99.99 percent DRE (Table IX).

All incinerators and industrial process kilns tested met or approached the RCRA HCl removal standard of 99 percent. Industrial boilers typically have no existing controls for HCl, but none exceeded the 1.8 kg/h emission standard because wastes with low net chlorine content were employed.

Achieving the RCRA particulate emission standard of 0.08 gr/dscf was a problem for a number of the incinerators tested by EPA. Four of the eight units tested failed to meet the RCRA standard. Two of those facilities were marginally above the emission limit and could likely meet the standard with minor operating adjustments. The remaining two facilities appeared to need significant design and/or operational changes.[86] In some cases, failure of the particulate emission standard may be attributed to dissolved neutralization salts in mist carryover from caustic scrubbers.

No significant changes in particulate emissions were observed for industrial boilers and certain of the industrial proess kilns when they fired waste fuels compared to emissions for fossil fuels only.[87,88] Some increased emissions were observed in kilns employing electrostatic precipitators for particulate control. These increases were attributed to changes in the electrical resistivity of the particles due to the presence of increased chloride levels. Adjustments in ESP operation should correct this in most cases.

Metal Emissions

Metals such as arsenic, barium, beryllium, chromium, cadmium, lead, mercury, nickel, and zinc are of possible concern in waste incineration because of their presence in many hazardous wastes and because of possible adverse health effects from human exposure to emissions. Incineration will change the form of metal fractions in waste streams, but it will not destroy the metals. As a result, metals are expected to emerge from the combustion zone essentially in the same total quantity as the input. The principal environmental concern, therefore, centers around where and in what physical or chemical form the metals end up in the combustion system, i.e., bottom ash, in APCD residues, or stack emissions.

Most interest has traditionally focused on stack emissions of metals. Increasing attention, however, is now being given to the quality of residuals from incineration of metal-bearing wastes since disposal of these materials may be subject to tough restrictions on land disposal under HSWA.

Metals present in the feed to combustion devices are typically emitted in combustion gases as particles rather than vapors. However, some of the more volatile elements (e.g., mercury and selenium) or their chemical compounds may be released to the atmosphere partially in the vapor state. The processes involved in the formation of particles are very complex and are only partially understood at present. Most of the current state of knowledge on metal behavior in combustion has come from research on coal combustion.[89-92]

In general, data on metal emissions and partitioning for hazardous waste incineration are limited and often incomplete. Organic emissions have been the focus of most historical emissions assessments of these facilities. Data on air pollution control device effectiveness for metals are even more scarce.

In 1982, Gorman *et al.* collected data on metal emissions from the Cincinnati MSD incinerator.[93] Metals data were also collected in three earlier tests sponsored by EPA in 1976.[94-96] The best source of metal emissions data, however, is the series of incinerator tests more recently conducted by EPA in support of the Regulatory Impact Analysis for the 1982 RCRA incinerator standards.[79] Average emission rates for these latter tests are shown in Table X. Actual values varied over a considerable range.

Wallace *et al.* recently reviewed all of the available metals emissions data for hazardous waste incinerators and compared them to emissions for other conventional combustion sources.[97] The five most frequently detected metals are Ba, Cd, Cr, Pb, and Ni. Hg was not found in any of the emissions, but this was because only particulate metal and not vapor was sampled in the studies. The relatively volatile metals (Sb, Cd, Pb) generally show enrichment in fine particulate emissions (i.e., higher concentration relative to their concentration on larger particles). This enrichment phenomenon is an important consideration for health assessment studies, since the fine particulates are also more likely to be inhaled.

Metal emissions from the hazardous waste incinerators tested were equivalent to those reported for municipal solid waste incinerators.[99] The emissions appear to be from two to 20 times higher than those from sewage sludge incinerators.[100] It is important to note, however, that it is difficult to extend the findings from these few tests to hazardous waste incinerators in general. This is because metal emissions are a function of the amount of metal input to the incinerator (which is highly variable day to day and facility to facility) as well as the efficiency of the incinerator in controlling metal emissions. Some of the incinerators tested, for instance, employed no air pollution control equipment.

Even where air pollution control equipment is used, it is difficult to draw conclusions on air pollution control system efficiency for metals because of the uncertainty of the sampling methods usually employed for control device input rates, the lack of particle size information and the relatively low quantities of metals available in collection samples. EPA is in the process of assembling a report on all of the available air pollution control device efficiency data for metals.[101]

Metals emissions may also be of concern for high temperature industrial processes employing hazardous waste as a fuel. Much of the test data in this regard are for waste oil combustion[102,103] in small boilers. Lead is the primary element of concern here since 50 to 60 percent of the combustion chamber input generally exits the stack. Stack concentrations of lead of 5,000 to 72,000 $\mu g/m^3$ have been observed in tests of small boilers of sizes ranging from 0.5 to 15 × 10^6 Btu/h.[103] EPA has promulgated rules controlling the metals level in used oils.[13] In addition, restrictions on waste metal content are being considered in proposed rules for industrial boilers and furnaces to be published in 1987.[14]

Table XI. Most frequent thermal destruction process stack emissions.

Volatile compounds	Semivolatile compounds
Benzene	Naphthalene
Toluene	Phenol
Carbon tetrachloride	Bis(2-ethylhexy)phthalate
Chloroform	Diethylphthalate
Methylene chloride	Butylbenzylphthalate
Trichloroethylene	Dibutylphthalate
Tetrachloroethylene	
1,1,1-Trichloroethane	
Chlorobenzene	

Combustion Byproduct Emissions

The current RCRA incineration standards regulate destruction and removal only for the major hazardous compounds in the waste. However, even under good combustion conditions, incomplete combustion byproducts may be emitted. One of the concerns expressed by some scientists and environmentalists regarding hazardous waste thermal destruction is the possible impact on human health and the environment of emissions of potentially hazardous products of incomplete combustion (often referred to as PICs). While many of the incinerator field tests conducted to date have attempted to quantify byproduct emissions, these data have been criticized as being incomplete and insufficient for the purposes of a full risk assessment.[46] Testing has focused largely on identification of Appendix VIII organic compounds only. Comparison of total hydrocarbon emissions with the total quantity of specific organic compounds identified in the emissions has revealed that only a relatively small percentage of the total hydrocarbon emissions may have been identified.[104]

Incomplete combustion byproducts from hazardous waste incineration have been recognized for some time. Early pilot-scale studies of the thermal destruction of the pesticide, Kepone, found emissions of hexachlorobenzene and several other "daughter products" which had been predicted from previous laboratory-scale studies.[105] Similar thermal decomposition studies followed for PCBs[106] and dozens of other compounds.[107-110]

While the RCRA incinerator standards do not currently regulate incomplete combustion byproducts, the earlier proposals did recognize and discuss this issue. The January 1981 Phase I rule proposed that emissions of incomplete combustion byproducts be limited to 0.01 percent of the POHC input to hazardous waste incinerators.[10] Although no final action was taken on that aspect of the rule, researchers, regulators, and environmentalists have pursued the question of PICs with great vigor since then, including various attempts to compare actual field performance results to the porposed standard.[111-113]

One of the basic problems in assessing the results of laboratory and, particularly, field studies of PIC emissions is the fact there is no standardized definition of what a PIC is. While a POHC is defined in the RCRA regulations, a PIC is not, in a rigorous sense. Thus, there is often confusion even among scientists working in the area. Strictly speaking, PICs are organic compounds which are present in the emissions from the incineration process, which were not present or detectable in the fuel or air fed to the incinerator. In EPA's test program, compounds were considered to be PICs if they were regulated organic compounds (i.e., listed in Appendix VIII of CFR 40 Part 261) which were detected in stack emissions, but not present in the waste feed at concentrations greater than 100 ppm.[111]

Compounds in the emission stream which are identified as PICs may actually result from any one of the following phenomena:

1. Compounds resulting from the incomplete destruction of the POHCs, i.e., fragments of the original POHCs.
2. New compounds "created" in the combustion zone and downstream as the result of partial destruction followed by radical-molecule reactions with other compounds or compound fragments present. These compounds may also result from the incomplete combustion of non-Appendix VIII compounds in the waste. This aspect may be especially significant where fossil fuel is used in incineration and where waste is fired into conventional industrial furnaces as only a percentage of the heat input.
3. An Appendix VIII compound originally present in the feed stream before incineration but not specifically identified as a POHC.
4. Compounds from other sources (e.g., ambient air pollutants in combustion air). In some field tests, compounds identified in the stack emissions as PICs were actually found to have come from contaminants (trihalomethanes) in the potable water used for scrubber water makeup.[111]

Given the complexity of sources of potential PIC compounds, it is not surprising that a consensus PIC definition has been difficult to achieve. Consequently, for the purpose of this review, it seems more productive to examine the issue of combustion byproducts separately from any type of specific definition by ignoring the source or cause of the emission of particular compounds and considering all organic compound emissions (including POHCs) as combustion byproducts (CBs). A recent EPA study has examined CBs in this fashion.[112] The study examined field test data from 23 EPA-sponsored emissions tests at thermal destruction facilities. Included were eight incinerators, nine industrial boilers, and six industrial kilns. Organic emissions from hazardous waste facilities were compared to emissions when these facilities were burning fossil fuel only. The organic emissions were also compared to organic emissions from municipal solid waste incinerators and coal-fired utility boilers.

The EPA studies of thermal destruction systems identified 55 Appendix VIII compounds (28 volatile and 27 semivolatile) in stack emissions. These compounds were emitted at normalized rates that span over five orders of magnitude, 0.09 to 13,000 nanograms of emissions per kilojoule (ng/kJ) of combustor heat input (one ng/kJ = 2.34×10^{-6} lb/million Btu).

The greatest number of compounds were emitted in the 10 to 100 ng/kJ range. Only nine of the 23 facilities emitted identified hazardous compounds at rates exceeding 100 ng/kJ.

The volatile compounds tended to be detected more often and in significantly higher concentrations than the semivolatile compounds. The compounds that occurred most frequently and in the highest concentrations, nine volatile and six semivolatile, are listed in Table XI. Emission rates for incinerators, boilers, and kilns are shown in Table XII for 12 of these compounds for which sufficient data are available for comparison. The data show that values from test run to test run varied considerably. Thus, these data do not allow prediction of levels for all three combustion devices. Many of the volatile compounds showed higher levels for boilers, and semivolatile compounds tended to be higher for incinerators.

Data were also available from several baseline (no waste firing) tests on boilers and kilns which allowed comparison of emissions from hazardous waste combustion with combustion of other fuels. While there was a wide range in values from test to test, the data suggested there is little inherent difference between waste and fuel combustion emissions.[112]

Sufficient data for five semivolatile compounds were available to compare their emissions when burning hazardous waste versus their emissions from municipal incinerators and coal-fired power plants. Similar data were not available for volatile compounds. Table XIII presents this comparison. The four phthalate compounds in the table all show very similar emission rates from all three sources. Naphthalene emissions were lower for power plants than the other two sources. Again, the data suggest that for these compounds there is little inherent difference between combustion sources.

Table XII. Emission rates of specific compounds from incinerators, boilers, and kilns, ng/kJ.[a]

	Incinerators		Boilers		Kilns	
	Mean	Range	Mean	Range	Mean	Range
Benzene	87	2–980	30	0–300	580	290–1,000
Toluene	1.6	1.5–4.1	280	0–1,200		No data
Carbon tetrachloride	0.8	0.3–1.5	1.8	0–7.2		No data
Chloroform	3.8	0.5–8.4	120	0–1,700		No data
Methylene chloride	2.2	0–9.6	180	0–5,800		No data
Trichloroethylene	5.2	2.3–9.1	1.2	0–13	1.3	0.7–2.8
Tetrachloroethylene	0.3	0–1.3	63	0–780		No data
1,1,1-Trichloroethane	0.3	0–1.3	7.5	0–66	2.4	(One value)
Chlorobenzene	1.2	0–6.0	63	0–1,000	152	33–270
Naphthalene	44	0.7–150	0.6	0.3–2.1		No data
Phenol	7.8	0–16	0.3	0–0.8	0.02	0–0.05
Diethylphthalate	3.7	2.8–4.8	0.4	0.04–1.6		No data

[a] Expressed as ng of emission per kJ of combustor heat input (1 ng/kJ = 2.34×10^{-6} lb/MM Btu).

Dioxin and Furan Emissions

Without doubt, the greatest amount of scientific and public attention has been given to one class of incinerator combustion byproducts, the dioxins and furans. The terms dioxin and furan refer to families of 75 related chemical compounds known as polychlorinated dibenzo-*p*-dioxins (PCDDs) and 135 related chemical compounds known as polychlorinated dibenzofurans (PCDFs), respectively. These compounds are not intentionally made for any purpose; they are unavoidable byproducts created in the manufacture of other chemicals such as some pesticides, or as a result of incomplete combustion of mixtures containing certain chlorinated organic compounds. Since the first published report of PCDD and PCDF emissions from a municipal incinerator by Olie *et al.*[114] a large number of studies have been carried out to examine this phenomenon, including work by Buser *et al.*,[115] Eiceman *et al.*,[116] Karasek,[117] Bumb *et al.*,[118] Cavallaro *et al.*,[118] and Lustenhouwer *et al.*,[120]

Table XIII. Semivolatile compound emission rates from hazardous waste combustion, municipal incinerators, and a coal power plant, ng/kJ.[a]

	Hazardous waste		Municipal waste		Coal power plant	
	Mean	Range	Mean	Range	Mean	Range
Naphthalene	17	0.3-150	71	0.4-400	0.5	0.06-1.8
Bis(2-ethylhexyl)phthalate	4.6	0-21	4.6	0.4-12	7.6	0.2-24
Diethylphthalate	1.2	0.04-4.8	0.5	0-0.9	2.8	0.4-5.7
Butylbenzyphthalate	3.7	0.7-23	No data		0.5	0.3-1.0
Dibutylphthalate	0.3	0-1.1	3.9	1.5-7.6	3.0	0.09-8.7

[a] Expressed as ng of emission per kJ of combustor heat input (1 ng/kJ = 2.34×10^{-6} lb/MM Btu).

Most of the interest has been placed on municipal waste incineration. A number of excellent summaries of field emission data have been prepared.[121-123] EPA has reviewed available PCDD/PCDF emissions data for a broad range of combustion sources including fossil fuel and wood combustion and a wide range of industrial furnaces,[124] and has reported the results of recent emissions testing at 11 additional facilities.[125]

Dioxin/furan emissions data are somewhat less available for hazardous waste incineration facilities. EPA tests have examined dioxin/furan emissions at five incinerators,[79] six industrial boilers,[126] and three calcining kilns employing hazardous waste as a fuel.[127-129] Data are also available from test burns at PCB incinerators.[130,131] Dioxin/furan emissions from these data sources are summarized in Table XIV.

Of the 17 facilities only five emitted detectable levels of PCDD or PCDF. None of the facilities tested was emitting detectable levels of the most hazardous isomer, 2,3,7,8-TCDD. The highest PCDD levels reported were for an industrial boiler using a creosote/PCP sludge as a fuel, where PCDDs were present in the waste feed.[126] In most cases, no PCDD or PCDF was detected in hazardous waste incineration emissions for the facilities tested. By comparison, PCDDs and PCDFs have been found in emissions from 22 municipal waste incinerators for which complete stack emissions data are available.[123] Average emissions of PCDD and PCDF (3,300 ng/m^3 and 2,700 ng/m^3, respectively), were nearly three orders of magnitude greater than the highest values reported for hazardous waste incineration units.

Ash and Air Pollution Control Residue Quality

Facilities which incinerate hazardous wastes containing significant ash or halogen content will generate combustion chamber bottom ash and various types of residues collected by subsequent air pollution control equipment. Under RCRA, these ashes and residues are generally classified as hazardous waste also. Thus, facility operators must assess the characteristics of these materials to determine the proper method of disposal. The principal contaminants of interest are heavy metals and any undestroyed organic material.

Most, but not all, operating hazardous waste incinerators which generate combustion chamber ash, quench the ash (usually in water) before discharge. Since air pollution control equipment using wet collection methods predominates incinerator practice, most additional ash and haloacid (e.g., HCl) is also collected in aqueous effluent from a scrubber, absorber, or wet ESP.

Only limited characterization data are available for combustion chamber ash and air pollution control residues.

Table XIV. Dioxin/furan emissions hazardous waste thermal destruction facilities (mg/m^3).

Facility type	Sample/(waste)[a]	2,3,7,8 TCDD	PCDD	PCDF	Reference
Commercial rotary kiln/ liquid injection combustion incinerator	FG/FA[b] (HW)	ND[c]	ND	ND-1.7	(80)
Fixed hearth incinerator	FG/FA (HW)	ND	16	56	(80)
Liquid injection incinerator	FG/FA (HW)	ND	ND	ND	(80)
Horizontal liquid injection incinerator	FG/FA (HW)	ND	ND	7.3	(80)
Incinerator ship	FG/FA (PCB)	ND	ND	0.3-3	(126)
4 lime/cement kilns	FG (HW)	ND	ND	ND	(127-129)
Fixed hearth incinerator	FG/FA (HW)	ND	ND	ND	(130)
Rotary kiln/liquid injection	FG (PCB)	ND	ND-48	0.6-95	(131)
Industrial boiler	FG/FA (PCP)	ND	75-76	ND	(125)
Industrial boiler	FG/FA (HW)	ND	0.64-0.8	ND	(125)
Industrial boiler	FG/FA (HW)	ND	ND	ND	(125)
Industrial boiler	FG/FA (HW)	ND	ND	ND	(125)
Industrial boiler	FG/FA (HW)	ND	1.1	ND	(125)

[a] Information in parentheses describes waste feed; HW = hazardous waste; PCB = polychlorinated biphenyls; PCP = pentachlorophenol waste.
[b] FG—flue gases analyzed; FA—flue gas particulate analyzed.
[c] ND—not detected.

Combustion chamber ash and scrubber waters were analyzed for several of the incinerators tested by EPA as part of the incineration Regulatory Impact Analysis (RIA) program.[79] Recently, ten additional incinerators were sampled to characterize ash and residues.[132]

In the RIA study,[79] incinerator ash and scrubber waters were analyzed for organic constituents. Only two facilities had ash concentrations of organic compounds at levels greater than 35 μg/g. When organic compounds were detected, they tended to be toluene, phenol, or naphthalene at concentrations less than 10 μg/g. The same compounds were also detected in scrubber waters, usually at concentrations below 20 μg/L.

The results of the recent ten-incinerator test program generally confirmed the RIA results.[132] While more organic compounds were detected across all of the facilities (19 volatile and 24 semivolatile compounds), levels in ash were typically at or well below 30 μg/g. One facility had a toluene concentration of 120 μg/g and phenol concentration of 400 μg/g. These levels were believed to have resulted from the facility's use of chemical manufacturing plant wastewater for ash quenching.

More compounds were detected in scrubber waters across the ten facilities than in the RIA study (nine volatiles and five semivolatiles) and in higher concentrations. Semivolatiles ranged from 0 to 100 μg/L while volatile compounds were much higher (0 to 32 mg/L).

Combustion chamber ash and scrubber waters were also analyzed for metals in both the RIA study and the ten-incinerator study. Detected concentrations varied widely and were a function of the amount of metal in the input waste stream at each facility and how the residues were processed. However, only three of 104 measurements of these metals in leachates from the residues and ashes exceeded allowable toxicity characteristic levels using the EPA's extraction procedure test (EP). If a leachate from a waste material exceeds these levels (CFR 40 Part 261.24), the waste will be designated as a hazardous waste.

Overall, the data from both test programs have suggested that very small amounts of residual organic compounds remain in incinerator ash and incinerator air pollution control residues. Thus, the destruction and removal efficiencies reported for incinerators are almost entirely a result of destruction, rather than removal, of organic compounds. Levels of metals in ashes and air pollution control residues varied widely but appear to generally not exhibit the RCRA toxicity characteristic. On the other hand, it should be recognized that available data represent short-term samples from less than 10 percent of the total hazardous waste incinerator population in the United States. Use of these data to project residue and ash quality for specific waste/incinerator combinations is not possible. Metal and organic concentrations are highly waste and facility specific. They will likely be influenced strongly by waste characteristics and by operating conditions (e.g., scrubber water recycle rate, solids residue time in the combustion chamber, and contaminants in scrubber water and quench make-up water).

Predicting and Assuring Incinerator Performance

Existing data indicate that well-operated hazardous waste incinerators and other thermal destruction facilities are capable of achieving high levels of organic hazardous material destruction which equal or exceed current RCRA performance standards. Putting aside arguments over the adequacy of the DRE standard for protecting public health and the environment, virtually any well-designed thermal destruction unit should be capable of demonstrating high DRE if sufficient operating temperature, oxygen, and feed control are provided. While convincing trial burn performance data can be presented, uncertainty and distrust may exist regarding the reliability of thermal destruction systems in day-to-day operation after a permit is approved and when regulators are not present. Little is known quantitatively about the impact of normal process upsets or failure modes upon emissions. This is often a concern of the public in hearings on permit actions.

Table XV. Parameters typically employed to trigger fail-safe corrective action for incinerators.

Parameter	Basis for corrective action Excess emissions	Worker safety	Equipment protection
High CO in stack gas	X		
Low chamber temperature	X		
High combustion gas flow	X		
Low pH of scrubber water			X
Low scrubber water flow	X		X
Low scrubber ΔP	X		
Low sump levels	X		X
High chamber pressure		X	
High chamber temperature		X	X
Excessive fan vibration			X
Low burner air pressure	X		
Low burner fuel pressure	X		
Burner flame loss	X	X	X

Currently, permit conditions are primarily based upon process operating conditions which are documented during the conduct of a successful trial burn; i.e., one which demonstrated that the facility achieved or exceeded the RCRA performance standards. These operating conditions are then also used to establish fail-safe controls for the facility, which designate corrective action to be taken in the event process operation deviates from the demonstrated set points. Corrective actions could include changing auxiliary fuel addition rates, shutting off waste feed, increasing combustion air flow, etc., to control emissions, or other actions to protect worker safety and process equipment.[32] Table XV shows typical shutdown parameters which may be used to trigger fail-safe controls.

Operating conditions (e.g., combustion temperature, O_2, and CO in stack emissions, etc.) must be used as surrogates for continued high destruction performance after the trial burn since there is currently no real-time method to determine DRE for specific POHCs. DRE can only be determined with certainty via expensive ($50,000 to $150,000), often multiday testing procedures. Analysis results may take weeks or months to complete. While EPA believes the current permit approach is reasonable and protective of public health and the environment, many argue that the availability of a real-time monitoring technique to detect process upsets and alert operators to automatically take corrective action would significantly increase public acceptance of thermal destruction technology.

Two general classes of performance estimation techniques exist. The first of these involves the use of compounds which are either identified in the waste or added to it to serve as "surrogates" for the destruction of other important compounds in the waste. The second approach involves the use of indicator emissions such as CO or unburned hydrocarbons to mirror waste destruction efficiency. Both concepts are used to some extent in incinerator permitting currently.

Surrogates

The surrogates concept involves identifying an easily detected organic compound which is more difficult to thermally destroy than any of the other hazardous compounds in a waste mixture. It is then assumed that if destruction efficiency for this compound is known for a given facility then all other compounds in the waste will be destroyed to at least that degree. This concept therefore involves developing an incinerability ranking of compounds.

The RCRA permit guidance for selecting POHCs in wastes actually employs this approach. However, the identification of compound incinerability has proven difficult and possibly unreliable. EPA has suggested the use of compound heat of combustion (ΔHc) as a ranking of compound incinerability.[12] This ranking method has received considerable criticism and alternative scales, which have also been criticized, have been proposed. These ranking approaches have been recently reviewed and compared by Dellinger.[133] They include autoignition temperature,[134] theoretical flame mode, kinetics,[135] experimental flame failure modes,[136] ignition delay time,[137] and gas phase (non-flame) thermal stability.[138] The rankings of compounds by each of these indices were compared to their observed incinerability in actual waste incineration tests in 10 pilot- and field-scale units.[133] Each index failed to predict field results except for the non-flame thermal stability method. This method, based on experimentally determined thermal stability for mixtures of compounds under low oxygen concentration conditions, showed a statistically significant correlation for the compounds evaluated.

While the low oxygen thermal stability concept appears promising, data are available for only 28 compounds. Correlation for other important Appendix VIII compounds over a range of compound concentrations will be necessary before the method can be used reliably for POHC designation or as a basis for establishing continuous monitoring systems for specific surrogate compounds.

As a result of the uncertainty over incinerability rankings, the use of "additives" is being considered for overcoming the limitations of the single POHC compound approach. This concept involves the addition of a single, well-characterized compound or small group or "soup" of compounds to a waste stream, with subsequent continuous monitoring of the emissions of the compound(s) to serve as a measure of destruction performance. Compounds such as various freons[139,140] and sulfur hexafloride SF_6 have been proposed.[141-143] Conceptually, these types of materials would be ideal additives since they rarely occur in hazardous wastes, can be detected in emissions using on-line instruments and are not likely to be formed as combustion byproducts.

Combustion byproducts formation has caused difficulty in interpretation of incinerability data for mixtures of conventional POHC candidate compounds.[141,144,145] While laboratory-scale studies have shown some promise, attempts in correlating field incinerator performance with additives behavior results have been inconclusive to date. Additional testing is needed.

Performance Indicators

Carbon monoxide (CO) and total unburned hydrocarbons (TUHC) are emitted from all combustion systems in varying amounts. Because CO is the final combustion intermediate prior to the formation of CO_2 in the combustion process, it has been used in the determination of combustion efficiency. Unburned hydrocarbon emission values do not include all incompletely combusted hydrocarbons. Rather this is an instrumentation-derived value resulting from the passage of gaseous emissions through a hydrogen flame ionization detector (HFID), which is commonly used with gas chromatographs. The HFID responds to the number of carbon-hydrogen and carbon-carbon bonds in residuals in the combustion gas. Because it does not respond to oxidized products such as O_2, CO, CO_2, and H_2O, it has been used as an indicator of residual fuel emissions.

Because CO is an indicator of the degree of completion of combustion and TUHC may be reflective of the amount of incompletely combusted material in the exhaust gas, these measures have been considered as possible indicators of incinerator performance. Continuous monitoring of CO is required by the RCRA incinerator standards for this reason. TUHC measurements, however, are not required.

The use of CO and TUHC in hazardous waste incineration has been studied by several groups[136,141,146,149] and criticized by others.[145,148] Waterland obtained pilot-scale data which indicated correlations of the fractional penetration of POHCs (1-%DRE/100) with CO and THC.[146] Kramlich *et al.* and LaFond *et al.*[136,147] found that increases in CO preceded increases in the penetration of POHCs in a laboratory-scale turbulent flame reactor as parameters such as air/fuel ratio, atomization and degree of thermal quenching were varied. At the same time, TUHC tended to increase as POHC penetration increased. In a test of a pilot-scale circulating-fluidized bed combustor Chang *et al.*[141] indicated that penetration of combustion byproducts appeared to be correlated with TUHC and that there were no instances of high combustion byproducts penetration without a corresponding increase in CO. The converse was not true, i.e., increases in CO were observed on some occasions without a corresponding increase in combustion byproduct penetration. POHC destruction efficiency was high throughout this series of tests and did not appear to correlate well with either TUHC or CO. Daniels *et al.*, although critical of the use of CO as a surrogate for POHC DRE or as an indicator of incinerator performance, presented data obtained from a full-scale rotary kiln, which in five out of six cases indicated increased POHC penetration with increased CO concentration.[148]

Analysis of the pooled data from the EPA incinerator test program revealed that there was no absolute level of mean combustion temperature, mean gas phase residence time or carbon monoxide emission concentration which correlated with achieving 99.99 percent DRE.[79] Residence times ranged from 0.1 to 6.5 seconds in the facilities tested. Temperatures ranged from 648°C to 1450°C. Carbon monoxide (CO) levels were as high as 600 ppm, but at most plants ranged from 5 ppm to 15 ppm. It was concluded that the relationships between DRE and these parameters are, in all likelihood, facility specific and that waste characteristics, waste atomization, and combustion chamber mixing likely play equally important roles in achieving high DRE. Timing, funding, and facility constraints, however, did not allow for collection of sufficient performance data under varying conditions at each site tested to allow for such relationships to be quantified. In particular, few of the test conditions produced DRE significantly below 99.99 percent.

Dellinger[145] has suggested that one reason for difficulties in correlating CO with DRE is that the assumed rapid oxidation of hydrocarbons to CO may not be correct for complex hazardous wastes containing large halogenated and heteroatom molecules. For these wastes, formation of stable intermediate organic reaction products may delay the production of CO. This delay would tend to distribute or move the CO production maximum relative to fuel (waste) destruction efficiency and tend to negate the usefulness of CO measurement in the region of 99.99 percent DRE. Hall *et al.* have conducted laboratory studies of CO formation versus compound destruction for several complex mixtures and found no correlation.[149]

Predicting Performance

Based on current knowledge it would appear that no single performance indicator or surrogate is sufficient as a predictor of organic compound destruction in incinerators. While low oxygen thermal stability data show promise as a predictor of compound incinerability, the data base is still not sufficient to extend this concept to POHC selection or to the development of standard POHC soups for trial burns or compliance monitoring. Data on additives are also insufficient to project a DRE correlation. CO may be useful in setting an upper bound condition on compound penetration (1-DRE), but there is no demonstrated "correlation" between CO emissions and DRE. Elevated TUHC emissions are indicative of an increase in incomplete combustion byproduct emission, but not necessarily a decline in DRE or even an increase in hazardous combustion byproduct emission, in part, because the HFID is less sensitive to halocarbon compounds.

One of the additional limitations placed upon attempts to correlate surrogates and indicators with DRE is the lack of a significant data base on incinerator operation under failure conditions. A failure condition can be defined as a normal or accidental operational deviation which results in failure of the facility to achieve a 99.99 percent DRE. Most of the field incinerator data used to make TUHC and CO correlations has been taken under steady-state operating conditions. The impact of failure modes such as nozzle clogging and kiln overcharging upon CO and TUHC emissions has not been adequately quantified, largely because of limitations on test time and funding and, in particular, permit constraints which prohibit off-design operation of facilities. EPA is, therefore, conducting failure-mode testing at its bench- and pilot-scale research facilities in Jefferson, Arkansas, Cincinnati, Ohio, and Research Triangle Park, North Carolina. Preliminary results from these tests have been reported recently.[150,151]

Table XVI. Total excess lifetime cancer risk to the maximum exposed individual for incinerator emissions.[167]

POHCs	10^{-7} to 10^{-10}
PICs	10^{-7} to 10^{-11}
Metals	10^{-8} to 10^{-5}
Total	10^{-8} to 10^{-5}

EPA has also conducted non-steady-state operational assessments at three boilers employing hazardous waste as a fuel.[152] The impact of typical non-steady-state operating conditions (e.g., start-up, soot blowing, load change) upon DRE, combustion byproduct emissions, CO, and TUHC was studied. While elevated CO emissions were observed at two of the sites under off-design operation, attempts to correlate DRE with CO, NO_x, and O_2 emissions were unsuccessful, largely because 99.99 percent DRE was achieved under both good and off-design operation. The testing, however, acknowledged some of the difficulties in conducting off-design studies. In some cases, the duration of the process transient to be studied may be shorter than the sampling time required to collect a sufficient sample to assess DRE. The large volume and high surface area (boiler tubes) in boilers tended to delay emissions of organics from one off-design test to the next, making it difficult to separate cause and effect. This so-called "hysteresis effect" may also cause difficulty to some degree in interpreting the results of studies of transient operation in incinerators.

More testing under non-steady-state is needed, particularly for incinerators. While attempts to correlate performance with single indicators and surrogates have been largely unsuccessful to date, taken in some appropriate combination they may prove useful as real-time indicators of the onset of process failure.

Environmental and Public Health Implications

Regardless of the apparent capabilities of hazardous waste incinerators to meet or exceed the RCRA performance standards, the ultimate public test involves demonstration that there is no unacceptable increase in public health risk from the emissions to the environment. While any of the emissions from an incinerator may potentially be of environmental interest, most attention has been directed toward air pollution emissions. This is because they appear to represent the most important source of off-site human exposure and there is no opportunity for secondary containment or treatment of emissions once they leave the stack. Ash and scrubber residues, however, are lower in volume and can be contained, examined, and if necessary, treated prior to discharge or disposal. In addition to chronic exposure to recurring emissions, there are also environmental and public health impacts which could result from potential single event or catastrophic emissions at incineration facilities.

Risks from Single Event Emissions

As with any industrial facility, there are risks from potential accidents at incineration facilities such as fires, explosions, spills of raw waste and similar single-point events. These events are probabilistic in nature and their evaluation in a risk assessment is handled differently from continuous pollutant emissions from stacks. For instance, the U.S. Department of Transportation maintains statistics on the frequency of releases of cargo from vehicular accidents involving trucks. For tank trucks of all types, for instance, this is estimated to be 0.35 releases per million miles traveled.[47] Similar values may be identified for accidents involving storage facilities and transfer operations.

Little specific information on these types of accidents is available for hazardous waste incineration facilities. Ingiwersen *et al.* evaluated the potential off-site impacts of five hypothetical accidents at a planned hazardous waste incineration facility.[153] It was estimated that no long-term adverse effects could be expected from chronic exposure for the nearest residents (0.5 miles) and that any effects due to acute exposures to the HCl emissions from the accidents were expected to be short-term and reversible. Actual accidents at an operating European facility have been documented.[154] Seven accidents occurred over an 11-year period. One employee was injured and no off-site effects were reported for any of the incidents, which generally involved storage and handling operations. EPA has also recently examined transportation and spill related risks for ocean-based incineration and found that these risks were greater than risks from incineration.[44] In the absence of accident data specific for incineration facilities, statistics from related industrial practice are probably adequate in assessing these risks.

Methods for Assessing Risks from Recurring Emissions

The major concern of this discussion is the risk associated with recurring air pollution emissions from incinerators. The assessment of risk to human health rather than environmental damage is generally believed to be of greatest interest. Four general steps are involved in assessing the impact on public health from stack emissions from an incinerator

- Identify the health effects of constituents of concern as a function of concentration level.
- Predict the concentrations of these constituents to which the public may be exposed.
- Estimate the health impact of these concentration exposures.
- Conduct an uncertainty analysis.

Identification of the constituents of concern in stack emissions and the health effects of these constituents, is, of course, a function of the waste streams and incineration facility of interest. In general, any of the constituents on Appendix VIII of the RCRA standards are of possible interest. However, other organic compounds frequently found in combustion emissions (certain polynuclear aromatics and polycylclic aromatic compounds) may be of concern also. The major health effects of concern are for low-level chronic exposure to these materials. These effects are generally carcinogenicity, mutagenicity, teratogenic or target organ toxicity (e.g., sterility, behavioral effects).

Predicting the potential levels of human exposure to pollutants requires information on the frequency, intensity, duration, and continuity of exposure.[155] Exposure assessment generally requires the use of mathematical models which simulate the transport and dispersion of emissions from the stack to the exposed population. Of the air dispersion models available, EPA has most often used the Industrial Source Complex Long-Term Model (ISC-LT) for predicting annual average concentration for hazardous waste incinerator facility studies.[156,157] The Oak Ridge National Laboratory has linked the ISC-LT model with computerized meteorology and population data bases and programs to form the Inhalation Exposure Methodology (IEM).[158,159] The IEM employs U.S. population data from the 1980 Census and local meteorological data along with ISC-LT to estimate air pollutant concentrations and human inhalation exposures in the vicinity of hazardous waste incinerators located anywhere in the United States. The IEM has been used extensively by EPA in assessing regulatory alternatives for hazardous waste incinerators.[160,161]

The exposure information generated by models such as the IEM may then be employed to estimate human health risk. The individuals at highest risk of developing adverse health effects are of most interest. The risk to this "maximally exposed population" is estimated from the modeled exposure at the point of highest annual average pollutant ground-level concentration outside the facility. For each exposed individual, cancer risk is expressed as the cumulative risk over a 70-year (lifetime) period of continuous exposure.

A variety of estimators are available to quantify the health risks of substances. Carcinogen potency factors have been developed by EPA based on assumed no safe level.[162] For noncarcinogenic effects, no observable adverse effect levels (NOAELs) have been used to derive reference dose (RfD) levels.[163]

There is considerable uncertainty involved in conducting risk assessment. Numerous assumptions must be made regarding pollutant emission levels, pollutant effects, dispersion factors, etc. Only a fraction of the needed tests of the effects of chronic, low-level exposures to environmental pollutants have been done. There is also considerable uncertainty in extrapolating effects from high doses which cause effects in animals to low doses in humans. Linearity assumptions are typically used in making such extrapolations. Some investigators have questioned the wisdom of such assumptions, however.[164]

Beyond this, very little is known about how, or even if, this information can be used to estimate the effects of complex mixtures of the substances usually present in incinerator stack emissions. For these reasons and other limitations, most assessments adopt assumptions and risk estimate values which produce an estimate of a worst case effect. In order to promote consistency in risk assessments, EPA has recently published in the *Federal Register* a six-part guidance on risk and exposure assessment methodologies.[165] This guidance is an excellent resource to those conducting or evaluating risk assessment studies.

Overall Risks from Long-Term Air Pollution Emissions from Hazardous Waste Incinerators

Risk assessment and risk management have been used increasingly by industry and government over the past 10 years in evaluating control technology and regulatory options for managing hazardous waste.[166] The initial 1978 RCRA incineration standards, for instance, were almost entirely design and performance oriented. In the 1981 proposal, however, EPA incorporated risk assessment into what was called the best engineering judgement (BEJ) approach to regulating and permitting incinerators.[10] The operating and performance standards for incinerators were to apply to facilities unless a site-specific risk assessment indicated that a higher degree of control was necessary. The risk assessment proposal, however, was not included in the final rule in 1982, largely because of concern from the regulated community over the uncertainty of risk assessment approaches. Rather, risk assessment and cost-benefit analysis became a more integral part of the development of hazardous waste control technology standards through the conduct of Regulatory Impact Analyses (RIA) of all proposed standards as required by Executive Order 12291.

A number of risk assessments have been conducted for specific hazardous waste incinerators and for incineration on a national basis. Using the results of emissions data from nine full-scale incinerator tests,[79] EPA conducted a risk assessment as part of its Incinerator RIA in 1982. The objective was to examine the economic impact of the regulations on the regulated community, and to estimate the health and environmental effects of the regulations.[167] The risks due to principal organic hazardous constituents (POHC), combustion byproducts (PICs) and metal emissions were developed (Table XVI).

While these results show that the human health risks from most incinerator emissions are low, risks from metal emissions show the greatest potential for exceeding a 10^{-6} cancer risk. The risks from metals emissions ranged up to two to six orders of magnitude higher than values for POHCs and PICs, and dominated the total risk values. Risks from residual POHC and PIC from the incinerators tested were low and were essentially equivalent.

Taylor *et al.* reported the results of a risk assessment for metal emissions using the same test data,[168] but employing somewhat different assumptions. Using the IEM methodology, carcinogenic and noncarcinogenic risks were examined. Interestingly, these results showed even lower cancer risks than the EPA study. Individual lifetime cancer risks for the maximum exposed population ranged from a low of 4.48×10^{-11} for beryllium to a high of 3.47×10^{-6} for chromium. Noncarcinogenic risks were also small. All values were well below the respective ADI (acceptable daily intake) values. Lead intake was highest, estimated at 2 percent of the ADI.

Kelly reported similar conclusions for a risk assessment of stack emissions from a hazardous waste incinerator in Biebesheim, West Germany.[169] Maximum ground level air concentrations for 24 metals (and for PCB) were estimated using the IEM. All levels (including PCB) were less than 2 percent of the corresponding continuous exposure limit (CEL) value.

Holton *et al.* examined the significance of various exposure pathways for air pollution emissions from three sizes of land-based incinerators located at three hypothetical sites in the United States.[170–172] For certain organic chemicals, the food chain pathway may be an important contributor to total human exposure. However, the study concluded that the human health risk from emissions was small for all of the chemicals studied irrespective of the exposure pathway.

Fugitive emissions from auxiliary facilities at incinerators (e.g., storage tanks) were also estimated to be an important contributor to total pollutant emissions.[171–172] Few studies have quantified fugitive emission levels at incinerators. The studies which have been done, however, have not shown that ambient levels are a cause for concern.[79,173,174]

The risks associated with incineration of hazardous wastes at sea have been recently compared to risks from land-based incineration.[47] While risks of marine and terrestrial ecological damage were estimated, the direct human health risks from stack emissions are of greatest interest in this discussion (Table XVII). The incremental cancer risk to the most exposed individual was determined for POHCs, PICs, and metals for two scenarios: a PCB waste and an ethylene di-

Table XVII. Incremental cancer risk to the most exposed individual by type of stack release.[47]

Systems	PCB waste	EDC waste
Ocean based		
POHCs	1.45×10^{-10}	5.51×10^{-10}
PICs	1.68×10^{-12}	3.36×10^{-9}
Metals	6.37×10^{-7}	1.06×10^{-6}
Total stack	6.37×10^{-7}	1.06×10^{-6}
Land based (two sites)		
POHCs	5.13×10^{-8}	1.43×10^{-7}
PICs	1.79×10^{-6}	2.59×10^{-8}
Metals	2.65×10^{-5}	3.12×10^{-5}
Total stack	2.74×10^{-5}	3.14×10^{-5}

chloride (EDC) waste. Not surprisingly, the human health risk of stack emissions from ocean incineration were less than those of land-based systems, largely due to distance from population. The land-based incinerator risk values were similar to those estimated in the EPA incinerator RIA. POHC and PIC releases showed low risk, generally one to five orders of magnitude less than those for metals. Risks from metals accounted for from 90 percent to almost all of the identified risk from either system, and exceeded the 10^{-6} risk level for only the land-based scenario. The study notes, however, that the assumptions used in the assessment overstate the likely levels of carcinogenic metals in the hypothetical wastes used in the assessment and, therefore, likely overestimate emissions and risk level.

In another study, Holton[175] compared the potential differences in human exposure to emissions from identical PCB incinerators in ocean and land-based contexts. Land-based incineration showed higher inhalation exposure. The only human exposure pathway considered for at-sea incineration was ingestion of contaminated fish and shellfish. Accidental spills were not assessed. Inhalation exposure for land units was two orders of magnitude higher, terrestrial food chain ingestion exposure was a factor of 20 higher, and drinking water ingestion exposure was estimated to be about the same as that for consuming fish and shellfish. No estimate of absolute risk was attached to any of the estimates.

All of these risk assessment studies point to a conclusion that stack emissions from incineration of hazardous waste pose little risk to human health. However, as previously stated, the emissions data base upon which many of the assessments were based has been criticized by the EPA Science Advisory Board (SAB) as being insufficient.[46] SAB has recommended that a more complete assessment of the quantity and physical/chemical character of incineration emissions be done to provide a basis for a more complete risk assessment than has been possible to date. The SAB points to the fact that only a portion of the organic mass emissions has been identified in past studies. Many believe that most of this unidentified mass is non-chlorinated C_1-C_5 hydrocarbons, which are of little concern from a risk standpoint. However, test data are only just beginning to emerge to confirm or disprove this belief. EPA has recently completed a full-scale incinerator emissions test where as much of the mass emissions as possible will be specifically identified. The testing included steady-state and typical upset conditions for a large rotary kiln incinerator. Results should be available by the summer of 1987.[176]

It is not clear, however, that even this level of emissions information will really answer the question of how much absolute risk is associated with incinerator emissions. From the standpoint of the lay public, it may be more useful and productive to compare these emissions with other types of combustion emissions whose risks we have accepted in daily life. Lewtas and others[177] have done interesting work on the comparative cancer potency of complex mixtures of pollutants (e.g., power plant emissions, automobile exhaust, cigarette smoke). Using short-term bioassays of organics extracted from actual emissions, the relative cancer potency of emissions has been estimated.

Comparative mutagenic emissions rates (expressed as revertants per mile or joule) have been determined from testing of mobile sources and stationary sources. Experimental work to date suggests that the mutagenic emission rates of wood stoves, for instance, are as much as four orders of magnitude greater than those for conventional coal-fired utility power plants.[177] It is also apparent from the data base that variations in organic emission rate affect the net carcinogenic emission rate more than variations in the carcinogenic or mutagenic potency of the emissions. Similar sampling and testing is needed for incineration emissions so that their potency can be compared to everyday sources such as wood stoves, oil furnaces, and utility power plants. It should be noted, however, that use of comparative mutagenic emissions rates alone does not account for variations in potential human health impact that occur due to differences in exposure level to emissions from sources of different types or as a result of different routes of exposure.

Conclusions

The body of knowledge concerning hazardous waste incineration has been expanding rapidly since 1980. This review has examined some of the most significant aspects of this information. A number of conclusions may be drawn on the status of incineration technology, current practice, monitoring methods, emissions and performance, and public health risks. Beyond these, a number of remaining issues and research needs can also be identified.

Based on this review, the following conclusions may be drawn:

1. Incineration is a demonstrated, commercially available technology for hazardous waste disposal. Considerable design experience exists and design and operating guidelines are available on the engineering aspects of these systems.
2. A variety of process technologies exist for the range of hazardous wastes appropriate for thermal destruction. The most common incinerator designs incorporate one of four major combustion chamber designs: liquid injection, rotary kiln, fixed hearth or fluidized bed. The most common air pollution control system involves combustion gas quenching followed by a venturi scrubber (for particulate removal), a packed tower absorber (for acid gas removal) and a mist eliminator. However, more than half of the existing incinerators employ no air pollution control equipment at all.
3. Uncertainty exists as to the exact scope of current hazardous waste incineration practice in the United States. Best information is available for 1983, when between 1.7 and 2.7 million metric tons of hazardous waste is believed to have been incinerated in 208 incineration units across the United States. As much as 47 million metric tons of incinerable waste was generated in 1983.
4. Implementation of HSWA and SARA as well as industrial concerns for limiting long-term environmental liability will encourage increasing amounts of hazardous waste to be directed to incineration facilities. While current capacity appears adequate, a near-term short-fall in commercial incineration capacity may develop, particularly for facilities which can handle hazardous waste sludges and solids.
5. The technology of stack sampling for trace organic compounds is relatively sophisticated. Considerable experience and attention to quality assurance and quality control are needed. Documented sampling and analysis methods are available for most of the parameters of

interest in incineration performance assessment. Methods have been validated for a number of compounds. With proper planning of test activities, detection limits are not a limiting factor in assessing incinerator performance.

6. Continuous emission monitors are available with adequate operating ranges for many of the combustion emissions of interest (CO, CO_2, O_2, TUHC, NO_x). However, continuous monitors for specific organic compounds are not available. No real-time monitor exists for measuring destruction and removal efficiency.
7. Incinerators and most industrial processes employing hazardous waste as a fuel can attain the RCRA destruction and removal efficiency requirement and the HCl emission limit.
8. Certain incinerators have had difficulty achieving the RCRA particulate matter emission limit of 180 mg/m^3. Data suggest that improved air pollution control technology or operating practices will enable these facilities to be upgraded to meet the standard, however.
9. Insufficient data are available on the fate of heavy metals in incineration systems and the efficiency of typical hazardous waste incinerator air pollution control equipment to control emissions of specific metals and their salts.
10. Insufficient data are available on the impact of typical upset or off-design operating conditions on incinerator and industrial furnace emissions.
11. Considerable uncertainty exists over the definition and significance of incomplete combustion byproducts. An insufficient data base exists on the full spectrum of potentially hazardous compounds which may be in incinerator emissions. Comparative emissions data for a limited number of compounds suggest that incinerator emissions are similar in character and emission rate to emissions from fossil fuel combustion.
12. Based on current data, chlorinated dioxin and furan emissions are not significant for hazardous waste incinerators. The most hazardous dioxin isomer (2,3,7,8-TCDD) has not been detected in emissions at 17 facilities tested for these compounds. Levels of all PCDD and PCDF emissions from hazardous waste incinerators are approximately three orders of magnitude less than those reported for municipal waste incinerators.
13. Limited data on incinerator ash and air pollution control residues suggest that organic compound levels are low and that destruction is the primary reason for high destruction and removal efficiencies, not removal. Metal concentrations in ash and residues vary widely, depending upon metal input rate to the incinerator and process operation (e.g., scrubber water recycle and make-up rates).
14. General process control systems and strategies exist to control incinerator performance. However, none of the available real-time monitoring performance indicators appear to correlate with actual organic compound DRE. No correlation between indicator emissions of CO or TUHC and DRE has been demonstrated for field-scale incinerator operations, although CO may be useful as an estimator of a lower bound of acceptable DRE performance. It may be that combinations of several potential real-time indicators (CO, TUHC, surrogate compound destruction) may be needed to more accurately predict and assure incinerator DRE performance on a continuous basis.
15. Available approaches for estimating compound incinerability have not corelated with field experience. The best approach appears to involve the use of experimentally derived non-flame thermal stability data. However, an insufficient data base is currently available to extend this method for use in revised guidance on POHC selection.
16. There appears to be little increased human health risk from hazardous waste incinerator emissions, based on assessments done to date. Metal emissions appear to be most significant in the risk values which have been derived. However, a complete assessment of all of the potentially hazardous materials in incinerator emissions has not been completed. This information is needed to enable a comprehensive risk assessment of incinerator emissions.
17. In spite of the demonstrated destruction capabilities of hazardous waste incinerators and the apparent low incremental risk of emissions, there is considerable public opposition to the siting and permitting of these facilities. Permits require three years to finalize, on average. Uncertainty over permitting and public acceptance will likely result in a near-term short-fall in needed capacity, particularly for commercial facilities which could incinerate solids and sludges.

Remaining Issues and Research Needs

While thermal destruction represents the most effective and widely applicable control technology available today for organic hazardous waste, a number of issues remain concerning its use in the long term. These include:

- Destruction effectiveness on untested/unique wastes
- Detection of process failure
- Control of heavy metal emissions
- Emissions of combustion byproducts
- Real-time performance assurance
- The role of innovative technology

Destruction Effectiveness on Untested/Unique Wastes

All of the performance data which have been used in the development and assessment of thermal destruction regulations and standards to date have been collected for waste/thermal technology combinations typical of current practice. However, the character of wastes which may be subjected to incineration in the near future will begin to change, perhaps dramatically. These changes will be influenced by EPA action to restrict many wastes from land disposal under the Hazardous and Solid Waste Act Amendments of 1984 and by increased emphasis upon remedial action at Superfund sites. Incineration will emerge as a feasible technological alternative for destruction of many of these wastes and site clean-up residues. However, EPA and industry will have considerably less experience in handling these wastes. Wastes will tend to have higher solids and water content, be more complex in their physical and chemical composition, have lower heating value, and/or potentially contain higher levels of hazardous metals and high-hazard organics compared to wastes which are typically incinerated today.

Consequently, while incineration is capable of achieving high levels of destruction for today's wastes, future practice may place new performance demands on current technology. For instance, 99.9999 percent DRE is now required for wastes bearing chlorinated dioxin and furan compounds. Many of these wastes appear at Superfund sites. EPA is also studying the need for heavy metals control regulations for incinerators. That effort may suggest the need for improved air pollution control systems or waste pretreatment.

Thus, performance testing of incinerators and other thermal destruction devices must continue in order to assure destruction and removal effectiveness for these untested wastes, to assess process limitations and waste pretreatment requirements, to determine the safety of process residues, and to improve our ability to predict incinerator performance on new waste materials.

Control of Heavy Metal Emissions

While the human health risk of incinerator emissions appears to be small, metal emissions have been the dominant component of the risk levels identified thus far. Metal emissions are controlled only indirectly by current standards through the RCRA incinerator particulate emission limit. The particulate standard, however, has proven difficult for a number of operating facilities to achieve. In addition, the metal content of wastes which may be subjected to incineration in the future may be higher as a result of the implementation of the HSWA land disposal restrictions and increased ultimate clean-up actions at Superfund sites. Consequently, while metal emissions may not pose a risk now, they may in future practice.

Insufficient data exist on the physical and chemical character of particulate matter generated by hazardous waste incineration systems. Few tests have examined the particle size distribution of emissions or the specific metal removal capability of the various air pollution control systems available. Likewise, insufficient data exist on the fate or partitioning of these materials in incineration systems. This information is needed to examine the potential impact of metals in wastes upon net environmental emissions and to evaluate various regulatory strategies which may be necessary to control increased emissions. These strategies could include metal input limits for waste or specific metal emission limits.

Emissions of Combustion Byproducts

Current information suggests that organic combustion byproduct emissions identified for incineration of hazardous waste do not represent a significant risk to public health. Some, however, have questioned the completeness of emissions data and, therefore, the adequacy of risk assessments performed using these data. This issue has emerged as a concern in numerous public meetings on incinerator permits and facility siting.

There is little doubt that none of the emissions testing efforts conducted to date has identified all compounds in incinerator stack emissions. The same is true, however, for virtually any other source of air or water pollution. Because hazardous waste facilities are perceived as being more hazardous than many other types of pollution control or industrial facilities, more attention is given to their emissions. Thus, while it is unlikely that any major, highly hazardous components of emissions have been overlooked, the data are not available to prove this to all who may be concerned. On the other hand, the task of finding all potentially hazardous compounds is an open-ended one, ultimately limited by expense.

Another issue concerning combustion byproducts emissions is that few tests have examined the level and chemical character of emissions for periods of time facilities may be operating under upset conditions (transients or failure modes). More experimental work is clearly needed here. Some testing has shown that there is little change in POHC DRE over significant operating ranges or under "apparent" failure conditions. At the same time, emissions of unburned hydrocarbons have increased. Research is necessary to determine if these "failure-mode" emissions pose a hazard.

One approach to resolving both the question of data completeness and failure mode impacts is to examine the relative potency of emissions using short-term bioassays and to use bioassay-directed chemical analysis as a means of more cost-effectively identifying the chemical compounds (perhaps previously unidentified) which are primarily causing the potency. While short-term bioassays have their own set of constraints and limitations, they have proven useful in comparing the cancer potency of mixtures of compounds from other combustion sources. Testing of a reasonable range of hazardous waste types under "good" and off-design conditions would give an indication of the range of potency of emissions as a function of operational conditions and in comparison with conventional combustion sources whose risks and character are more familiar to the general public.

Real-Time Performance Assurance

Once the public health significance of incinerator emissions is verified, methods must be available to assure that effective operation is maintained. A variety of surrogates and indicators of incinerator performance are being evaluated. None is fully satisfactory and little evaluation has been done under true failure conditions.

It may not be possible to find a set of easily monitored parameters which "correlate" with incinerator performance. However, it may be possible to identify parameters which may be sufficient to identify the onset of process failure. Research is necessary to examine the suitability of existing real-time monitoring systems and approaches to reliably predict process failure. Availability of such techniques may have a significant impact upon public acceptance of these facilities and form a technical basis for more effective compliance monitoring by regulatory agencies.

Role of Innovative Technology

A wide range of innovative hazardous waste technology has emerged since the passage of RCRA.[178] A number of these technologies are thermal destruction processes. The potential destruction capabilities and cost-effectiveness of these processes has been well publicized, although many of the techniques must be considered to be only in the developmental stage.

Many argue, particularly in public hearings, that decisions on permitting conventional incineration facilities should be postponed in favor of adopting more innovative approaches, whose inventors often claim higher destruction efficiency at lower cost than conventional systems. For specific waste streams (e.g., contaminated soils, PCBs), a number of innovative systems have demonstrated DREs equivalent to those of conventional systems. Some systems appear to offer advantages for handling specific (although sometimes limited) waste streams. Considerable uncertainty exists as to the true cost-effectiveness of some systems, since practical field experience is often not yet available to aid in identifying operating limitations.

Many of these emerging systems will find a role in future hazardous waste management strategies. Policy makers, public officials, and industrial decision makers should be careful, however, in delaying action on currently available, demonstrated, thermal destruction systems until the need, benefit, and operability of such innovative systems are clearly established.

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Background

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